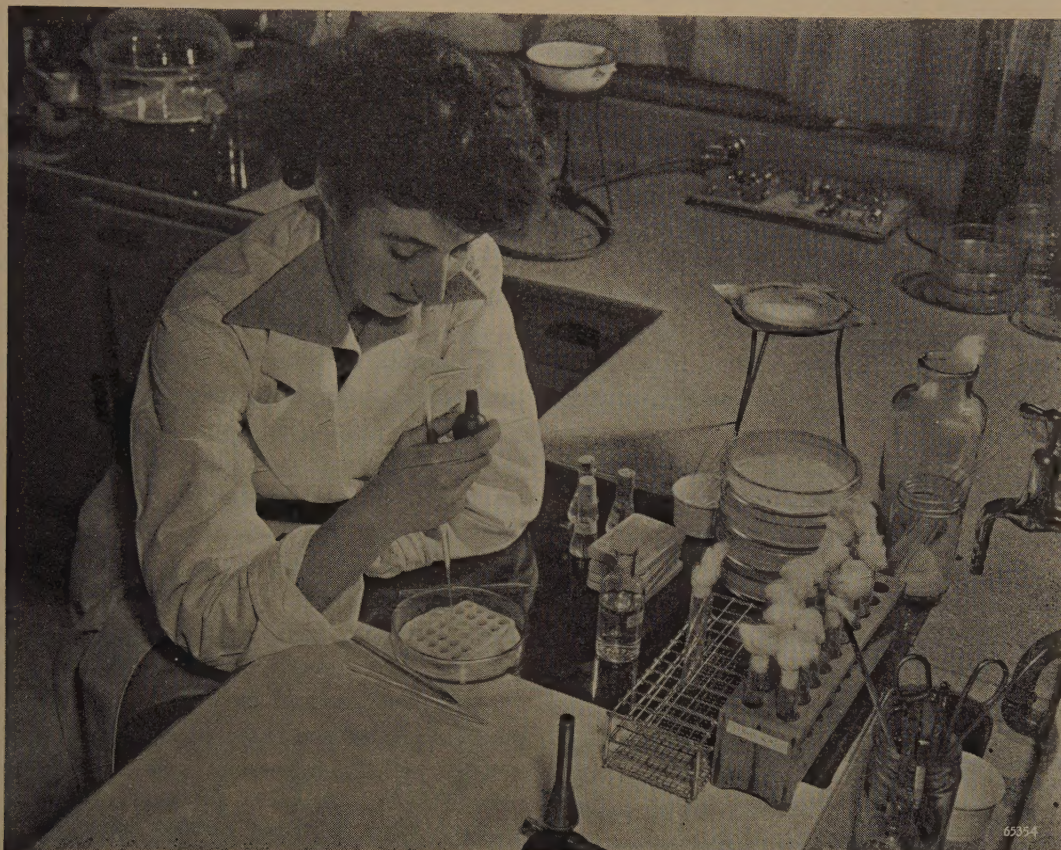


Philips Technical Review

DEALING WITH TECHNICAL PROBLEMS
RELATING TO THE PRODUCTS, PROCESSES AND INVESTIGATIONS OF
THE PHILIPS INDUSTRIES

EDITED BY THE RESEARCH LABORATORY OF N.V. PHILIPS' GLOEILAMPENFABRIEKEN, EINDHOVEN, NETHERLANDS



THE MANUFACTURE OF VIRUS VACCINE AGAINST INFLUENZA

by A. J. KLEIN *) and E. HERTZBERGER *).

616.921.5-085.371

*For some time now a branch of the Philips Industries has been making Vitamin-D preparations **). During recent years this branch has developed into a many-sided industry turning out pharmaceutical products such as insulin, preparations of liver and hormones, plant-hormones, insecticides, weed-killers, etc. It is now engaged upon the production of virus vaccines, a peculiar form of mass production taking place partly in some large egg hatcheries and promising to be of great importance not only for the Netherlands but also far beyond its frontiers.*

Influenza as an epidemic

A number of infectious diseases occurring in the form of epidemics, such as cholera, plague, typhoid, smallpox, etc., have lost their grip on

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mankind thanks to counter-measures evolved by medical science. These counter-measures consist on the one hand in the prevention of infection by certain hygienic precautions and on the other hand

**) See A. van Wijk, Lamp manufacture and vitamine research, Philips Techn. Rev. 3, 33-39, 1938.

in the immunization, by means of sera or vaccines, of individuals liable to infection.

During the last ten years it has been made possible to combat also influenza in this way. This disease often occurs in more or less harmless forms and as a result the public at large tends to underestimate its seriousness. The terrible epidemic of influenza that spread over the whole world in 1918 and 1919 and cost about 20 million people their lives is, however, evidence enough to show how important it is to have the means of combating this disease. Moreover, the seriousness of influenza is not to be judged solely from the number of deaths it causes. Influenza epidemics with low mortality figures, occurring, as they do, every other year or so, cause great losses to the national economy owing to the high percentage of workers laid up for weeks on end.

The possibility now offered of immunizing either certain individuals or whole groups of the people against influenza is therefore a great boon both from the medical as well as the social-economic point of view.

In this article something will be said about the principles underlying the preparation of the vaccine for immunization against influenza, the methods for the large-scale production of this vaccine and in particular those employed by Philips-Roxane at Weesp in Holland, and about the manner in which the vaccine is to be used in the event of an epidemic.

Immunization; serum and vaccine

What are the principles underlying immunization against an infectious disease?

The disease is caused by a morbidic germ, in the form of a bacillum or a virus, getting into the body and very rapidly multiplying itself. The body reacts to this by producing specific antibodies rendering the morbidic germs harmless. Roughly speaking the process of the disease can then be regarded as a contest between the morbidic germs and the antibodies; if the former multiply themselves at a faster rate than the latter are produced then they win, whilst in the other case the patient wins and recovers. If a person is already carrying a quantity of the specific antibodies before the morbidic germ gets into his body, then as soon as there is an infection that person has a good start, so to speak, and better chances of throwing off the attack — he is more or less “immune” to the disease.

One can become immune in three ways:

(a) Once a person has had an attack of the disease and fully recovered from it there is usually a sur-

plus of antibodies left in the body and this surplus continues to be active for a time, so that one is naturally immune against another attack for some length of time and possibly, in the case of some diseases, for the rest of one's life.

(b) A person can be injected with a dose of antibodies taken from some other persons or from test animals who have passed through the process of the disease; a preparation of antibodies sufficiently concentrated for this purpose can usually be extracted from the blood of a test animal, and this supplies the preparations known as “sera” or anti-sera.

(c) The body of the person to be immunized can be incited to prepare antibodies without rendering that body ill. This is done by injecting a “vaccine”, i.e. a preparation of inactivated germs. It is indeed surprising that this should be possible, considering that the morbidic germ is “killed” and can no longer multiply itself, but it is nevertheless still capable of bringing about the production of the specific antibodies. In fact it is not so surprising when it is borne in mind that there are also “dead” substances (proteins) capable of causing the formation of corresponding “antibodies” in the human body. Anyhow this method is probably the most important weapon available to the physician in combating epidemics, more so than the serum method. Since it has not yet been found possible to extract antibodies in the pure state for any disease, and only for a few diseases is it possible to extract them in strong concentrations, usually rather large quantities of a serum (some tens of cm³) have to be injected and owing to the sensitivity of the human body for foreign proteins this not infrequently gives rise to complications. For vaccination, on the other hand, usually only a few drops of the vaccine are sufficient because of the high concentration in which it can be produced, thanks to the multiplying power of the morbidic germs (not yet inactivated!). Furthermore, antibodies taken from other people, and especially when they are taken from animals, being “generic-foreign material”, are fairly soon expelled from the human system, so that the protection afforded by a serum (passive immunity) is of short duration — at most six weeks — whereas “active” immunity obtained by vaccination may last many months and even years.

The influenza virus

It is only possible to prepare a vaccine (and also a serum) after the germ causing the disease concerned has been identified, or rather — in the case

of the morbidic germ being unknown — after it has been possible to isolate it. Such was first possible in the case of influenza in 1933, when Smith, Adrewes and Laidlaw¹⁾ succeeded in extracting in a more or less pure form a virus from the liquid used by influenza patients for gargling. Test animals infected with this virus “caught” influenza. While the patients were recovering these investigators also succeeded in detecting in their blood antibodies against the virus found; test animals injected with virus preparations previously mixed with the blood extract did not become ill.

Further investigations carried out by a number of research institutions in America, Great Britain, the Netherlands and other countries proved that in the case of influenza it is not a matter of one morbidic germ but that there are several different “strains” of virus, distinguished, *inter alia*, by the fact that they cause the formation of different antibodies. According to their degree of relationship these strains of virus can be classified under a few groups which have been named influenza-A-virus, influenza-A'-virus and influenza-B-virus. A virus can be neutralized not only with its own antibody but also with antibodies of other viruses belonging to the same group. The practical importance of this fact will be explained later. Suffice it to say here that a number of laboratories now have preparations of the isolated strains of virus at their disposal, from which by cultivation they are able to produce the quantities of virus required for experiments and for the manufacture of vaccines and anti-sera.

Fundamentals of the preparation of virus vaccine

In essence the cultivation of a virus consists in causing it to multiply itself in a suitable medium. With the object of vaccination, this cultivation is necessary for two reasons: firstly, the extraction, purification and concentration of a virus from the excretions of influenza patients is a cumbersome process and yields only comparatively small quantities, whilst secondly it has been proved that for an effective immunization highly concentrated vaccines have to be used. Prior to 1941 such highly concentrated vaccines were not available and this is the reason why the first attempts to immunize groups of the population met with little success, although with mice and ferrets — the test animals mostly used for this work — a decided immunizing action of the inactivated virus preparations had been observed immediately.

The cultivation of a virus on any large scale was a problem never encountered before. Good methods were known for cultivating all sorts of bacteria, e.g. in bouillon or blood which may be made into a solid culture medium with agar-agar, at certain temperatures. One of the essential differences between a bacillum and a virus, however, is that the latter can only multiply on or in living tissues. The customary simple culture media for bacteria were therefore unsuitable and use had to be made of test animals or of tissues derived from test animals and kept alive in a suitable medium (mostly of rather complicated composition, i.e. the so-called tissue cultures). For a time the virus was cultivated, for instance, in the lungs of mice. This technique was far too cumbersome for the large-scale production of vaccine, and the purification (removal of undesirable proteins) and sterile preservation of the product (exclusion of foreign germs which would take part in the multiplication and make the vaccine useless) were difficult problems. Consequently the result could not be called satisfactory.

An excellent idea, which eliminated at once most of the difficulties, was to use embryonated chicken eggs as medium for the cultivation²⁾. Here we have indeed a living tissue, easily obtainable at all times in large quantities, contained in a shell guaranteeing sterility — veritably the egg of Columbus. When this idea came to be further investigated it appeared that with a suitable choice of the spot inside the egg also an excellent opportunity was afforded for the purifying of the virus solution obtained. Since 1940 very effective methods have been developed upon this principle for the cultivation of influenza virus. It is such a method — worked out for the greater part empirically — that is being employed in the mass manufacture of influenza virus vaccine by Philips-Roxane at Weesp (Holland).

Before proceeding to describe the details of the method followed, it is to be pointed out that the cultivation of the virus is only one of the steps in the preparation of the virus vaccine. Other essential steps are: the purifying of the virus, its inactivation, possibly drying, and last but not least the assay and dilution. These processes, too, will be briefly described.

Incidentally, it may be mentioned that once the technique of manufacturing a virus vaccine has been mastered the possibility of immunization also against other diseases caused by a virus comes within the reach of the medical profession. A vaccine

¹⁾ W. Smith, C. H. Adrewes and P. P. Laidlaw, *Lancet* 225, 66, 1933.

²⁾ W. Smith, *Brit. J. Exp. Path.* 16, 508, 1935.

can be made against parotitis (mumps) for instance, the methods for the preparation of which are entirely analogous to those followed for influenza vaccine.

Manufacture of the vaccine

Cultivation of the virus in embryonated chicken eggs

Fig. 1 is a cross section of a fertilized chicken egg after ten days' incubation (hatching normally takes 21 days). The most favourable part of the egg for the development and subsequent purification of the virus is the membrane of the allantoic cavity. This cavity, filled with the clear allantoic fluid, almost entirely envelops the embryo and takes up all the waste products while the embryo is developing, thus acting, as it were, as its bladder. On the tenth day of incubation the virus is injected into this cavity, where in two days' time it multiplies about 100,000 fold. In this way, from one or two eggs (according to the strain of the virus) an amount of virus is obtained sufficient for immunizing one person.

An enormous number of eggs are therefore re-

quired for manufacturing vaccine on a scale calculated for the immunization of a whole population. The incubation of the eggs for the required period of ten days and the cultivation of the virus during

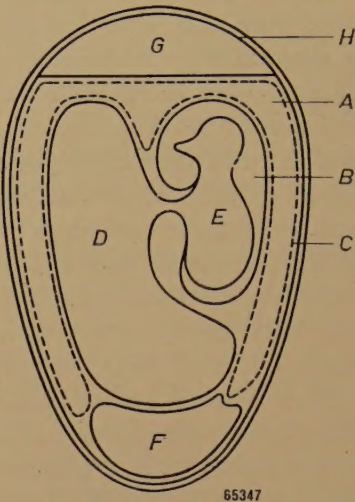


Fig. 1. Diagrammatic cross section of a fertilized chicken egg after 10 days' incubation. E embryo, D yolk sac, B amnion cavity, A allantoic cavity, C allantoic membrane, F albumin, G air space cell, H shell membrane.



Fig. 2. Machine for the simultaneous hatching of 16,000 eggs. The temperature inside the cabinet is maintained at a level of 37.5 °C. At the bottom are trays of water providing for the necessary humidity of the air, so that the eggs do not lose any of their liquid through the pores of the shell. The trays filled with eggs are placed in a large drum which can be rotated through an angle of 90 degrees: in one position of the drum the eggs are tilted 45° to one side and in the other position 45° to the other side. This turning of the eggs (in imitation of what the brooding hen regularly does) has to be done every day to prevent the heaviest parts of the egg from settling at the bottom of the shell. A wooden framework rotating around the drum provides for a uniform distribution of the heat and moisture content of the air inside the cabinet.

two days is therefore done in large incubators such as are used in the poultry-raising industry, each having a capacity of, say, 16,000 eggs (see *fig. 2*).

After three days' of incubation all eggs are examined in a darkened room, one by one, in a strong beam of light from a mercury lamp (see *fig. 3*). *Fig. 4* is a picture of a fertilized egg as examined in this way; the blood vessels formed during the first three days of incubation are clearly seen. At this stage it is thus possible to see whether an egg has been fertilized or not, and those that have not been fertilized are rejected. After ten days' incubation the eggs are examined again and marked at the spots where "inoculation" and "harvesting" is to be done. This is necessary because the eggs are inoculated by drilling a small hole in the shell and then injecting a few drops of a virus preparation: when this is being done care has to be taken not to puncture one of the blood vessels. The laboratory assistant examining the egg therefore marks it with a cross at a point suitable for the injection at the right height and at a safe distance from the blood vessels. Before injection takes place a second small hole has to be made in the air space of the egg (see *fig. 1*), so that as the virus is injected a corresponding amount of air can escape. For the subsequent harvesting the boundary of the air space is also marked out on the shell at this second examination of the egg.

The drilling of the holes is illustrated in *fig. 5* and the process of injection in *fig. 6*. Injecting is done in a glass-top case with two openings through which the assistant can pass her arms. After the inoculation the two holes in the egg are sealed with



Fig. 3. Examination of the eggs in a strong beam of light to see whether they have indeed been fertilized; the same devices are also used for marking the eggs for subsequent inoculation and harvesting.

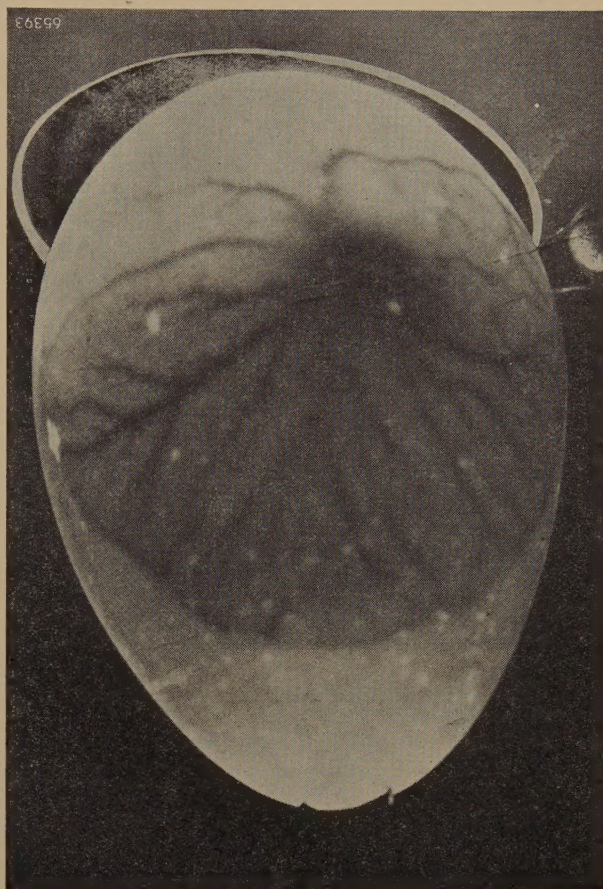


Fig. 4. An egg as seen when examining it after three days' incubation. The blood vessels are clearly seen. The boundary of the air space cell cannot be seen on the photograph owing to the halo effect.

paraffin wax. Inside the case is a germicidal lamp (the TUV lamp), the ultra-violet rays from which keep the air and everything else inside the case sterile³); it is of the utmost importance that no living bacteria or active undesired viruses on the egg shell or on the point of the injection needle should get into the egg and there multiply together with the influenza virus (of course at this stage the influenza virus itself must not come under the germicidal action of the lamp rays). To keep the air inside the case sterile in spite of the arm holes, a certain pressure is maintained in the case by means of a ventilator; the stream of air entering at the back passes through a filter, where all dust is filtered out, past a second germicidal lamp and thus in a perfectly sterile condition into the work compartment, from which it flows out through the arm holes (see *fig. 7*).

³) For a description of these lamps and their operation see J. Voogd and J. Daams, Inactivation of bacteria by ultraviolet radiation, *Philips Techn. Rev.* **12**, 111-119, 1950 (No. 4).



Fig. 5. The necessary holes are drilled in the eggs with a kind of dentist's drill.

There is not much to be said about the actual process of cultivation, which takes place in two days after the injection of the virus into the egg. It is rather peculiar that the best results are obtained when the incubating temperature during the cultivation period is kept at 36.5°C , whilst the normal incubating temperature, maintained during the first 10 days of incubation, is 37.5°C .

After the two days' cultivation the eggs are kept 24 hours in a refrigerator, so that the embryo dies off and the rest of the contents of the egg "sets" more or less, this being desired for the "harvesting". For the harvesting the part of the egg shell covering the air space is cut off without damaging the contents of the egg. Then with a pipette, connected via a flask to a water-jet pump, the liquid contents of the allantoic cavity are drawn off into the flask. This, too, is done in a sterilized case with arm holes, at which a number of laboratory assistants work together (see fig. 8). One flask can contain the culture from about 300 eggs.



Fig. 6. The case, kept sterile with TUV lamps, in which the incubated eggs are inoculated with the virus to be cultivated. The glass top does not allow the rays of the 2537 \AA wavelength to pass through. The arm holes can be moved a little to the side to provide a comfortable position for the assistant's arms.

After sterilization by heating, the eggs from which the allantoic fluid has been extracted can be worked up into cattle food.

The virus preparations required for the inocula-

tion of the eggs are kept in a refrigerator and by cultivation, likewise on incubated eggs, in a small thermostat (miniature incubator) can be constantly renewed.

Purifying and assaying the virus preparation

For purifying the virus, that is to say the removal of most of the undesired proteins present in the solution that has been collected, a process is applied which might be called "differential centrifugation". In a fairly large, normal, centrifuge with a speed of 3000 r.p.m. the flocculent precipitates from the virus solution are deposited on the wall of the machine. The remaining liquid containing the virus is run through a small centrifuge rotating at a very high speed (Sharples super-centrifuge, 50,000 r.p.m.); see *fig. 9*. This centrifuge is highly selective, all the molecules over a certain weight — and those only — being deposited on the wall. Thus the virus (which in this connection can be regarded as a heavy protein molecule) is deposited on the wall of the rotor in an extremely pure state, being subsequently shaken off with a suitable liquid. The speed of the centrifuge and the rate of flow have to be very precisely adjusted and continually checked,

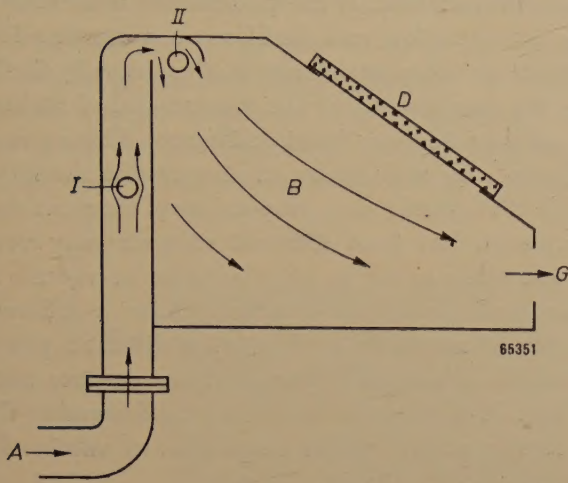


Fig. 7. Cross-sectional diagram of the inoculating case. The work compartment *B*, with glass top *D* and arm holes *G*, is kept sterile by the TUV lamp *II*. A certain pressure is maintained inside the case by the admission of filtered air at *A* with the aid of a ventilator. This air is sterilized as it passes the TUV lamps *I* and *II* and leaves the case through the arm holes.



Fig. 8. Case, sterilized with TUV lamps, in which the cultivated virus is extracted from the eggs. Each of the assistants working at the case uses a pipette, connected to a suction pump, with which the liquid is drawn out of the allantoic cavity of the "decapitated" egg into the flask standing in the middle of the case. This flask can hold the culture taken from 300 eggs. In each suction line is a small intermediate flask which has to be inverted after every fourth egg for its contents to be transferred to the big flask. If one of the eggs happens to be a failure (for instance through a blood vessel bursting) the intermediate flask is replaced by a clean one, so that the contents of the big flask are not spoiled.

so as to ensure the right sedimentation. Since, during the flow of the liquid through the centrifuge, outside air is apt to be drawn in (see fig. 9b), also the centrifuge is set up inside a case sterilized with the aid of TUV lamps (fig. 10).

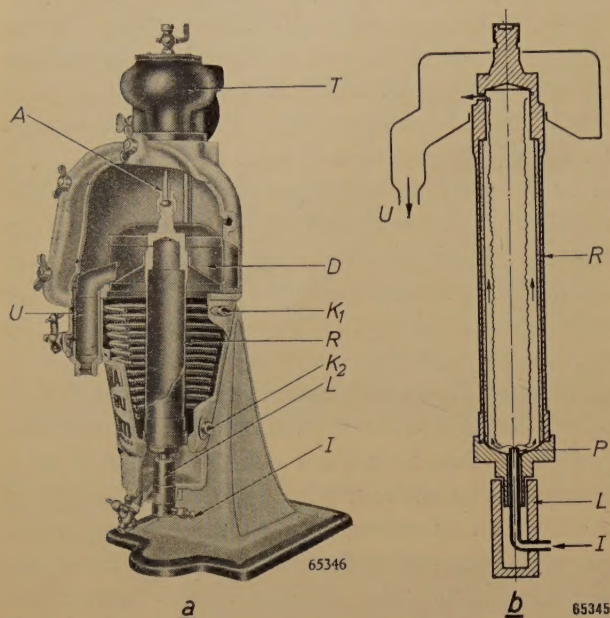


Fig. 9. a) The Sharples supercentrifuge. *T* driving steam or compressed-air turbine, *A* shaft rotating at 50,000 r.p.m., *R* rotor mounted on the shaft and through which the liquid to be centrifuged flows, *I* inlet, *U* outlet, *D* cover, *L* bearing leaving sufficient play for the rotor to find its own ideal axis of rotation, *K*₁ and *K*₂ water inlet and outlet for the cooling coil. In *b*) the sedimentation in the rotor (drawn very roughly) is made a little clearer. The liquid entering the rotor at *P* follows the rotation of the rotor almost immediately.

The highly concentrated virus preparation thus obtained is shaken with a small addition of formaldehyde, thereby completely inactivating the virus. After adding a preservative (sodium ethyl-mercuri-thiosalicylate) the virus solution can be kept in a refrigerator until it is needed.

Another method of preparing the virus for storage is by drying. Of course the water cannot be expelled from the solution by heating because then the virus is damaged. Boiling under reduced pressure is not practicable either, because then too much virus is lost (owing to excessive heating, concentration of salts or other causes). Very good results are obtained, however, by freezing the virus solution (in a vessel cooled with carbon dioxide) and then evaporating the ice by connecting the vessel to a vacuum pump. The dry residue containing the virus is then kept in a refrigerator at a temperature of -20°C .

The last, and very important, step in the manufacture of the vaccine is the determination of the activity of the suspension (assaying) and the dilution to the desired strength.

There is a simple method of determining the concentration of an influenza-virus suspension, namely the Hirst test ⁴⁾. This is based upon the discovery that influenza-virus suspensions cause the red blood corpuscles of chickens to clump. This phenomenon allows of the quantitative measuring of the concentration, and the Hirst test has therefore become an indispensable means of continually checking the manufacture of the vaccine and of making the desired dilutions (see frontispiece). This cannot, however, be said to be an assaying in the strict sense of the word: virus suspensions of the same concentration but from different cultures may vary considerably as far as their activity as vaccine is concerned, since the virus may have a different degree of antigenic action, i.e. a different power (retained or originally possessed) to produce antibodies. It is therefore necessary to determine the activity of the virus suspension as vaccine by means of test animals.

This is done according to the method prescribed by the National Institute of Health in the U.S.A., which has also been made compulsory by the State Institute of Public Health in the Netherlands. A number of mice are inoculated with different doses of the vaccine and after 14 days samples of their blood are taken. This blood serum is mixed with active influenza virus and dripped into the nostrils of non-inoculated mice. The serum from the vaccinated mice should neutralize the active virus, in which case the mice to which the mixture has been administered will stay alive. The dose of vaccine just neutralizing the virus is taken as the standard strength on which further dilutions are to be based.

This assaying is done also in the laboratories at Weesp. To conclude the preparation of the vaccine the prescribed tests are carried out — partly on animals — for making sure that the vaccine does not contain any living virus, any living germs of some other genus, or any other harmful substances of whatever nature. Not until then can the vaccine be released for medical use.

This is not the place to go into the manner in which the vaccine is injected into human beings. All that need be said here is that the persons to be vaccinated must not be oversensitive to chicken protein. Fortunately this is only the case with about 0.5% of the population, and any over-

⁴⁾ So long as a virus cannot be completely isolated it is of course not possible to determine its quantity by weighing, so that one has to have recourse to such means as biological effects, specific absorption of light or fluorescence, or suchlike.

sensitiveness (allergic reaction) can be determined by first injecting a very small dose into the skin (the actual vaccination is by subcutaneous injection).

Combating influenza with the virus vaccine

The fact that in the case of influenza it is not a matter of just one single virus but of various strains is of great influence in the combating of the disease. It cannot be known in advance what strain of the virus will be responsible for a future epidemic.

case of a "monovalent" vaccine. This is to be deprecated on account of the undesired secondary reactions, which in any case have to be limited to a minimum, and the more so because with a given capacity of the factory producing the vaccine only one third of the number of people can be immunized which otherwise could be treated with a monovalent vaccine.

Furthermore, it may happen that the epidemic is caused by a strain of virus as yet entirely unknown, a mutant such as seems to appear fairly

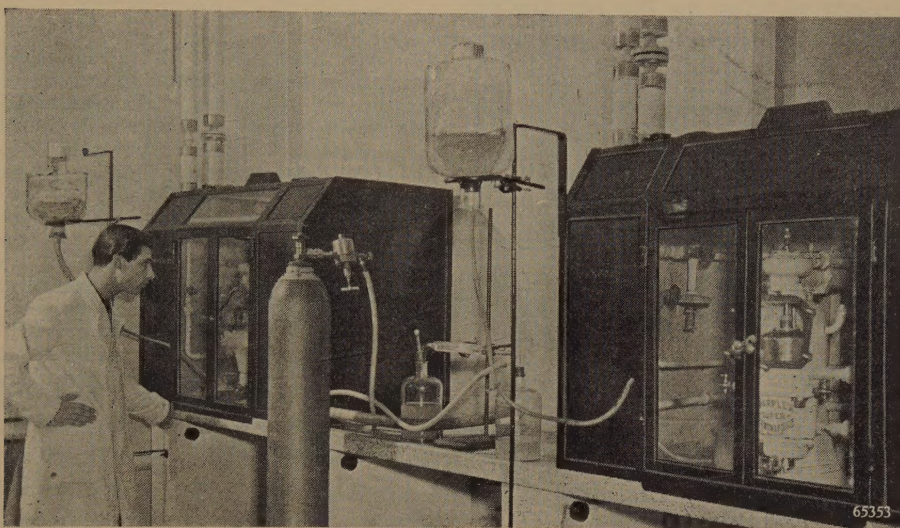


Fig. 10. Cases, kept sterile TUV lamps, in which the Sharples supercentrifuges are mounted. The centrifuges have to be easily accessible because at regular intervals the speed has to be checked and if necessary corrected.

Therefore, to make an influenza vaccine which can be held in readiness to cope with the first attack of an approaching epidemic or, in normal times while there are still no signs of an epidemic, to safeguard against possible future infection people for whom influenza involves particular risks, this vaccine has to be "polyvalent", that is to say it has to contain various suitably chosen strains of virus which together have the widest possible antigenic action.

To hold in readiness this polyvalent vaccine is not, however, an ideal solution. It is true that in the event of an epidemic breaking out the majority of the people vaccinated will be safeguarded against the infection if they have been vaccinated early enough and if the strain of virus causing the epidemic is susceptible for one of the antibodies created. But if the polyvalent vaccine is made up, for instance, from a mixture of three strains then every person has to be inoculated with three times the amount of vaccine that would be needed in the

regularly every ten years and which may not react at all to the antibodies formed by the polyvalent vaccine. In that case everyone who has already been vaccinated has to be revaccinated.

With a view to this situation, in 1948 the World Health Organisation established a service for reporting to all countries any outbreak of influenza in any part of the world and for taking immediate steps to isolate and identify the virus. Thus, in all countries to which the epidemic may be expected to spread in the course of some time it is now possible to proceed at once to the production of a monovalent vaccine against the identified morbid germ of the disease.

This means that the industry making the influenza vaccine is obliged to equip itself for coping with very heavy "peak loads". In order to meet this requirement without involving the installation of large permanent plant that would be standing idle most of the time, Philips-Roxane have estab-

lished a remarkable organisation. The manufacture of the virus vaccine depends for a large part on the use of large incubators for hatching the thousands of eggs needed. Such incubators, however, are already available in the poultry industry, where as a rule they are idle for several months of the year, just in the summer and autumn when epidemics of influenza commonly break out. It has therefore been arranged with several hatcheries in the country (from whom the fertilized eggs for cultivating the vaccine are procured) for their machines to be used in the vaccine production process in case of need. By temporarily increasing the number of assistants making up the inoculating and harvesting teams (the inoculating teams work in the hatchery, whilst for harvesting the eggs are transported to the factory) the production capacity can now easily be raised to a multiple of the normal.

Even with such a greatly increased capacity it is still impossible, within the short time available before the reported epidemic spreads to the country, to produce sufficient vaccine for immunizing the whole population. But then, after all, this is not really necessary. Much harm can already be avoided by immunizing those groups of people most exposed to the infection and certain individuals whose incapacitation would help the epidemic

to spread and thus aggravate the general dislocation of public services and industry. The vaccine available will therefore be reserved in the first place for the vaccination of doctors, nurses and suchlike, for personnel of electricity works, telephone exchanges and the foodstuffs industry, further for people living or working in communities, such as the military forces, seamen, pupils in boarding schools, workers in large factories, etc. For the same groups of people a preventive vaccination in normal times might also be considered. This would have to take place every year, because between 6 and 12 months after the injection immunization begins to decline.

Summary. As is the case with other infectious diseases, immunization is now also possible against influenza. The vaccine, a concentrated suspension of the inactivated influenza virus, is being manufactured on a large scale by cultivating the virus in the allantoic cavity of embryonated chickens' eggs. The injection of the virus into the egg, the cultivation and the harvesting of the greatly multiplied virus, as also the purification of the virus suspension and the assaying for correctly dosing as vaccine are described in this article. Since there are a number of strains of the influenza virus, in normal times a polyvalent vaccine is made containing a mixture of different strains and thus offering immunization against various strains of the virus. With the approach of an epidemic of influenza the specific strains of virus responsible for it is reported by an international organisation to the threatened countries, where steps can immediately be taken for producing a monovalent vaccine against that particular strain and vaccinating the population as far as necessary and possible.

THE ELECTRICAL RECORDING OF DIAGRAMS WITH A CALIBRATED SYSTEM OF COORDINATES

by B. G. DAMMERS, P. D. van der KNAAP and A. G. W. UITJENS.

621.317.755: 621.3.012

The construction of diagrams from a series of measurements demands the closest attention and takes a considerable time. Electronic engineering in recent years has enabled the construction of calculating machines which can take over some of the work of the human mind, and it also offers the possibility of constructing an apparatus which can very quickly take measurements and record their results in the form of a diagram.

Several articles have already appeared in this journal describing apparatus by means of which diagrams or graphs can be traced on the screen of a cathode-ray tube ¹⁾²⁾.

The tracing of such diagrams is done by periodically varying the "independent variable", measured by means of a proportional voltage, from the minimum to the maximum value. The "dependent variable" (also measured electrically) then likewise varies periodically through a certain range. After amplification these two voltages are applied to the horizontal and vertical deflection plates of a cathode-ray tube, thereby producing a curve on the screen.

In the apparatus described here, a calibrated system of coordinates in the form of a lattice is produced on the screen simultaneously with the tracing of the diagrams. This allows of an accurate numerical interpretation of the curves, which with the apparatus hitherto employed was more difficult and less accurate, owing to the lack of calibrating points.

Although this diagram-tracing apparatus can also be used for many other variables that can be measured electrically, this article will only deal with its application for recording the characteristics of electronic valves, where the quantities to be measured are already voltages or currents. This apparatus has proved to be of great value in the electronic-valve development department, where new types and modified forms of valves are frequently being examined.

Compared with the usual method of constructing a diagram point by point from meter readings, the use of the cathode-ray tube for this purpose

has the advantage that a curve can be plotted very quickly. This is highly important when, in the case of static measurements, the valve is likely to be overloaded and consequently damaged.

As was the case with the apparatus previously described, a family of I_a - V_a curves is simultaneously recorded for different values of the grid voltage of the valve. For this purpose, with the apparatus referred to in footnote ¹⁾, the grid voltage was rapidly changed in steps with the aid of a rotating commutator. Here this mechanical method of switching has been replaced by an electronic system, in view of the higher switching frequency required for the simultaneous tracing of the coordinate lattice. In place of the "impulse tube" employed by Douma and Zijlstra²⁾, normal amplifying valves are used.

Principle

The main parts comprising the diagram-tracing apparatus are indicated in the block diagram of *fig. 1*. The anode of the valve T under test receives from an alternating-voltage generator G , and a direct-voltage source V_a , a periodically changing positive voltage. This voltage is also applied to the horizontal deflection plates of the cathode-ray tube K via a deflection amplifier A_H . The voltage across the resistor R in the anode circuit is applied to the vertical deflection plates of K , also via an amplifier (A_V). Thus the coordinates of the spot describing a curve on the screen due to the changing anode voltage and anode current are at any moment proportional to the instantaneous values of these two electrical quantities.

The circuit also contains direct-voltage sources V_{g2} and V_{g3} , for applying the correct voltages to the screen grid and the third grid of the valve, and a step-voltage generator V_g supplying to the control grid a series of different direct

¹⁾ H. van Suchtelen, Applications of cathode ray tubes IV, Philips Techn. Rev. 3, 339-342, 1938.

A. J. Heins van der Ven, Testing output valves, Philips Techn. Rev. 5, 61-68, 1940.

²⁾ Tj. Douma and P. Zijlstra, Recording the characteristics of transmitting valves, Philips Techn. Rev. 4, 56-60, 1939.

voltages, so that a family of I_a - V_a curves for different values of the parameter V_g are traced at short intervals.

The tracing of the set of curves is alternated by the tracing of the lines of the coordinate lattice. This is made possible by connecting at the point b_2 in the leads to the deflection amplifiers A_H and A_V electronic switches (not shown in fig. 1), which will be discussed later.

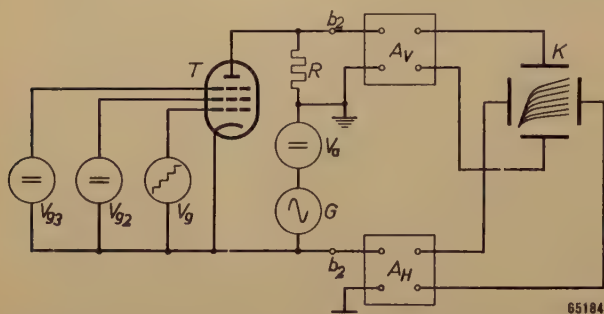


Fig. 1. Block diagram of the apparatus for measuring characteristics. T valve under test; V_a rectifier for supplying the anode direct voltage; G alternating-voltage generator for scanning the I_a - V_a -characteristic; R resistor across which a voltage is developed proportional to the anode current of the valve T ; K cathode-ray tube; A_V amplifier for the vertical deflection of the beam; A_H amplifier for the horizontal deflection; V_g step-voltage generator for supplying the control-grid voltage of T ; V_{g2} , V_{g3} rectifiers for the auxiliary grid voltages of T .

The tracing of the lines of the lattice is done in a similar way to the tracing of the curves, with this difference that one of the two deflection voltages is kept constant while the other varies periodically, in this case sinusoidally.

Twenty-five complete pictures (curves with lattice) are displayed per second. Each picture period is divided into four parts of 1/100 second, called quarters. In the first quarter the vertical lines of the lattice are traced, in the third quarter the horizontal lines, and in the second and fourth quarters the curves that are to be measured.

The three pairs of signals, viz. for the horizontal and vertical deflection (a) of the characteristics, (b) of the vertical lines of the lattice, and (c) of the horizontal lines, are conducted by three pairs of channels to the previously mentioned two electronic switches, which pass the pairs of signals in turn to the two deflection amplifiers of the cathode-ray tube.

The direct-voltage components of these three signals take part in the amplification up to the output of the electronic switch, thus making it possible to compare the direct-voltage components of the three pairs of signals: when there is any inequality in the switched voltages then, upon

switching over, a voltage surge occurs at the output of the switch, and this causes a discontinuity in the curve traced on the screen; where there is no such discontinuity this indicates that the switched voltages are equal.

This possibility is used for calibrating the lattice of coordinates, by comparing the direct voltage required for each line of the lattice with an accurately known, constant, direct voltage, as will be explained when describing the calibration.

Beyond the switches only the alternating-voltage components are amplified by the two deflection amplifiers, so that the centre of the picture is automatically brought into the centre of the screen of the cathode-ray tube.

As already observed, switching is done by means of two identical electronic switches, H and V , periodically passing the necessary signals to the horizontal and vertical deflection plates (see fig. 2). These switches each have three channels with picture-signal inputs b_1 , b_2 and b_3 and three switching-signal inputs s_1 , s_2 and s_3 . The three channels for the picture signals are periodically opened and closed by square-wave pulses, supplied by the switching-signal generator G_1 , being applied to the switching-signal inputs. The picture signals for the lattice are supplied by a step-voltage generator G_2 and an alternating-voltage generator G_3 with a fairly high frequency (7020 c/s). The form of the pulses produced by the three generators is shown in fig. 2. The switching-signal generator G_1 supplies negative pulses for opening the picture channels. In the first quarter the channels 1 are opened, the plates for the horizontal deflection receiving a step-voltage from G_2 and those for

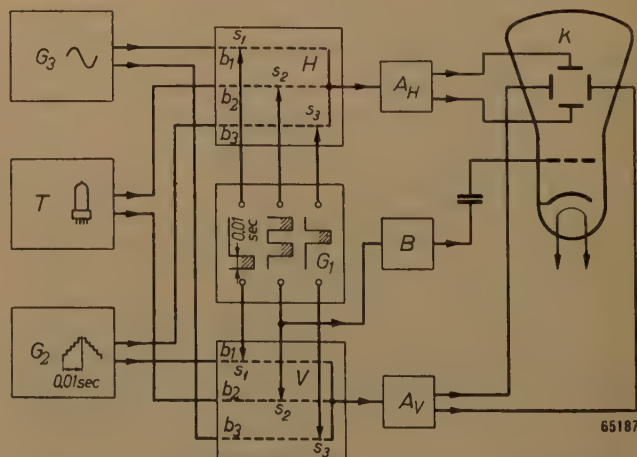


Fig. 2. Basic principle of the diagram tracer. H electronic switch for the horizontal deflection; V ditto for vertical deflection; G_1 switching-signal generator; G_2 step-voltage generator; G_3 7020 c/s generator; A_H amplifier for the horizontal deflection; A_V amplifier for the vertical deflection; B intensity control; K cathode-ray tube; T valve under test.

the vertical deflection a sinusoidal voltage from G_3 . A series of vertical lines are then traced on the screen of the cathode-ray tube.

In the second and fourth quarters the channels 2 are opened and the curves are traced. In the third quarter the channels 3 are opened, the plates for the horizontal deflection receiving a sinusoidal voltage and those for the vertical deflection a step voltage, thereby tracing a series of horizontal lines on the screen.

The variation of the voltages on the two pairs of deflection plates is shown diagrammatically in *fig. 3*, where it is assumed that only one curve is being traced.

As we have already seen, for the tracing of the lattice, step voltages are used. In the case where 13 lines (12 intervals) are traced the frequency in the succession of the steps is $13 \times 50 = 650$ c/s. The amplifiers have to amplify a considerable number of harmonics of this frequency with equal gain; the frequency band of the amplifiers is,

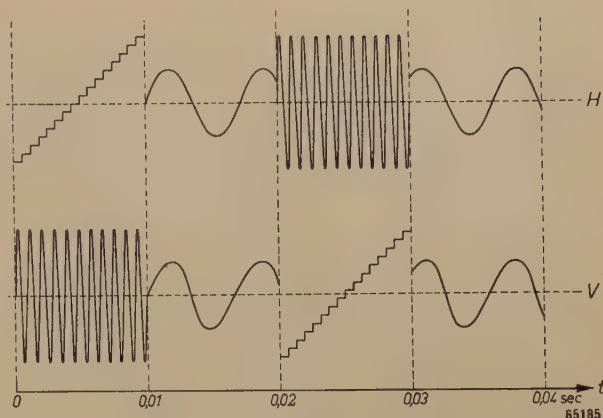


Fig. 3. Waveform of the deflection voltages when tracing one curve with a lattice of coordinates. H voltage on the horizontal deflection plate; V ditto for the vertical deflection.

of course, limited in width, so that it is advisable to keep the frequency of the steps as low as possible, thus to choose the smallest possible number of pictures per second. The lower limit of the picture frequency is determined by the persistency of

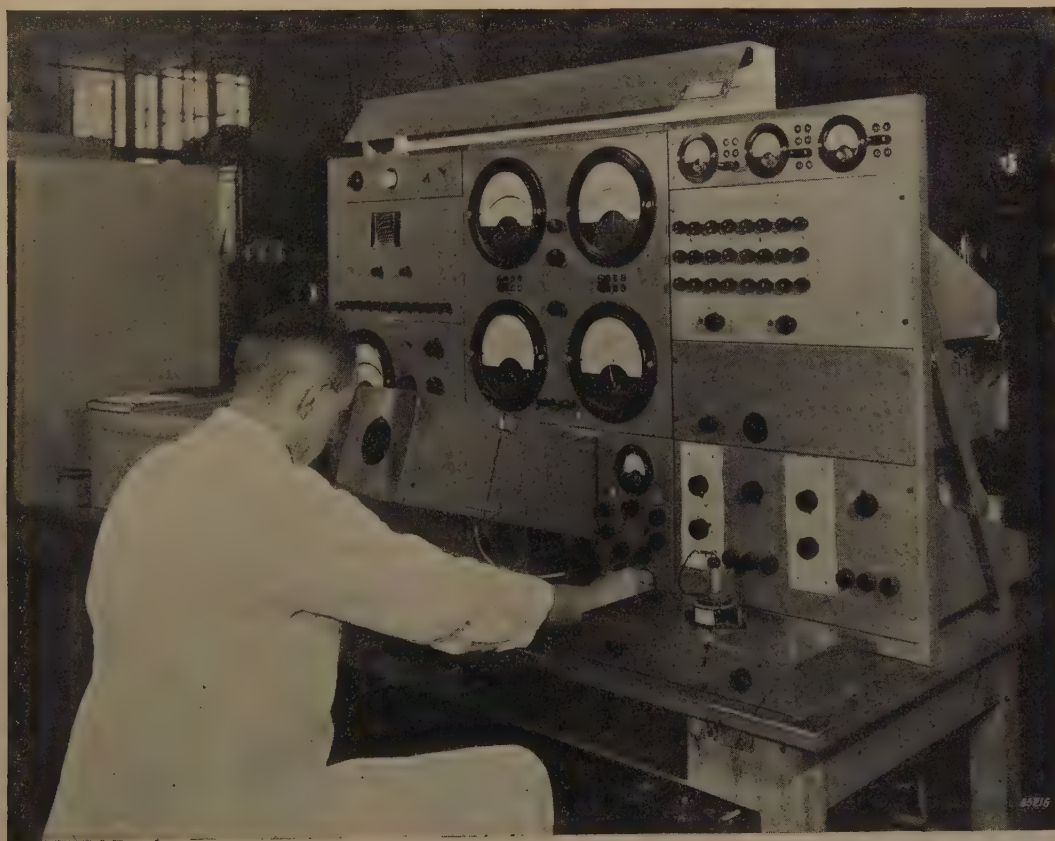


Fig. 4. Measuring and control panels of the diagram tracer. In the middle at the bottom the metal case containing the cathode-ray tube, type DW 16-2. On the bench on the right the valve under test. At the top on the middle panel the meters recording the filament current and the screen-grid voltage of the valve under test. On the right-hand panel at the top control meters for the screen-grid current, anode current and anode voltage, and underneath these the controls for adjusting the steps of the step-voltage generator for the lattice. On the left-hand panel at about the same level are the controls for adjusting the steps of the step-voltage generator supplying the grid voltage for the valve under test.

the screen and of the visual impression and also by the linearity in amplitude and phase of the amplifiers and electronic switches at low frequencies; 25 c/s has been found to be a good compromise.

In the block diagram (fig. 2) an "intensity control" B is indicated. This allows of the brightness of the lattice being varied with respect to that of the family of curves. If no special measures were taken, the curves — when there are only a few in the series — would be much brighter than the lattice and as a consequence the photographic recording of the picture on the screen would be over-exposed. To avoid this a square-wave control signal is applied via an amplifier to the grid of the cathode-ray tube, by means of which the intensity of the beam is reduced during the second and fourth quarters. This control signal has the same form as the signal that is used for opening the picture-signal channels.

The whole installation is contained in panels mounted in racks on a testing bench, a photograph of which is given in fig. 4. On the right of the bench is the valve under test, and in the middle of the bench, at the bottom, is the metal case containing the cathode-ray tube. The observer sitting at the bench views the screen of the tube through the opening, in front of which a camera can be placed.



Fig. 5. Rear view of the measuring and control panels of the diagram tracer. On the right at the top the step-voltage generator for the grid voltage of the valve under test, and on the left at the top the step-voltage generator for the lattice.

Fig. 5 is a back view of the panels. Underneath the bench are the supply units and the 200 W generator for scanning the characteristic of the valve under test.

The component parts of the installation are all made as easily replaceable units, the connections between which are made with the aid of plugs and sockets. Since the whole of the apparatus contains more than 200 electronic valves, with an average life of 10,000 hours, an average of one breakdown per 50 hours has to be taken into account. Spare units are therefore provided for quick replacement.

The electronic switches

Each of the switches, as we have seen, contains three channels. In one such channel there are two valves, the switched valve T_1 and the switching valve T_2 (see fig. 6).

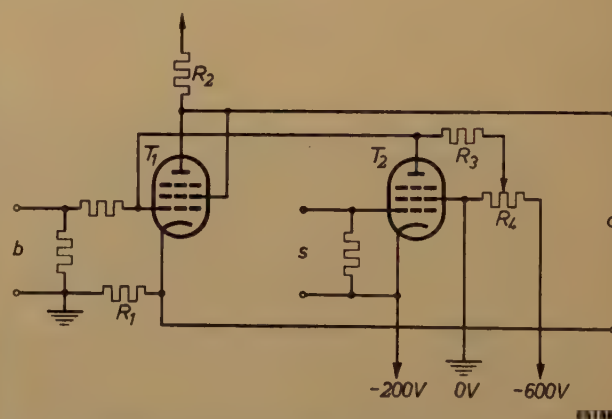


Fig. 6. Principle of the electronic switch circuit. T_1 switched valve, T_2 switching valve, b signal input, s switching-signal input, c signal output connected to the deflection amplifier.

For electronic switching a pentode is usually employed, and a positive pulse is applied to the second grid during the period that the valve has to transmit the switched signal. However, in the event of interferences arising in the switching pulses, this will affect the amplification factor of the switched valve and, therefore, the signal transmitted.

With the method employed for this apparatus the valve T_2 is cut off during the interval that the switched valve T_1 is conducting. The control grid of T_1 then receives via the resistor R_3 and the potentiometer R_4 a negative bias from a stabilized supply unit of -600 V.

During the interval that the valve T_2 is open, T_1 is cut off. The grid of T_1 , which is connected to the anode of T_2 , then has a voltage only slightly higher than the cathode voltage of T_2 , which is

at a potential of -200 V with respect to earth. Fluctuations in the switching impulse at s , although strongly influencing the negative control-grid voltage of T_1 , are not transmitted, because T_1 is cut off.

The correct working voltage for T_1 can be adjusted with the potentiometer R_4 . The three parallel-connected valves T_1 , one of which is always open and two cut off, have common cathode and anode resistors R_1 and R_2 , so that the signals entering the three channels at b leave the switch through the common output c .

of negative voltage pulses lasting $1/100$ second. In order to avoid hum trouble these signals are synchronized with the mains frequency (50 c/s): any hum interference arising in some way or other in the amplifier would lead to distortion of the picture on the screen of the cathode-ray tube. The signals being synchronized, any interference will only manifest itself in a slight curving of the lattice lines, which is not troublesome; if the signals were not synchronized the interferences would be manifest in a wave travelling right along the lines,

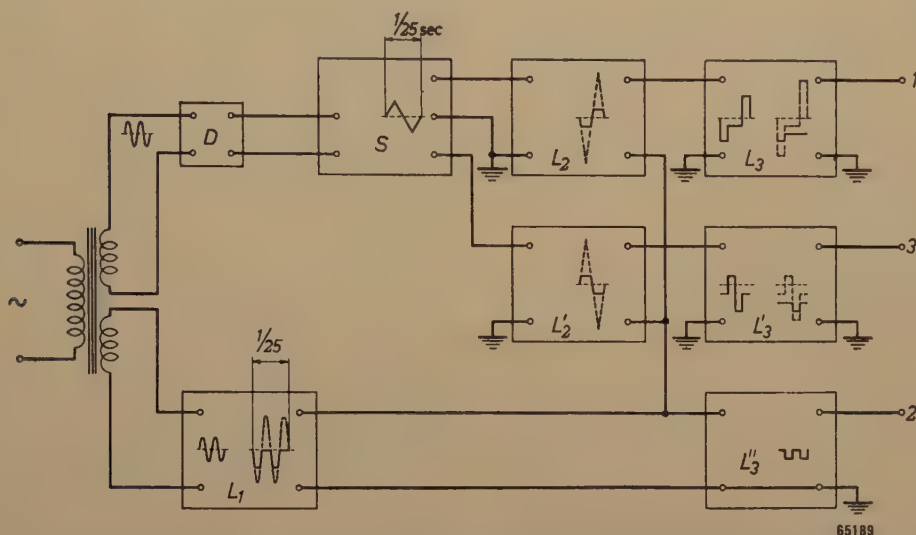


Fig. 7. Block diagram of the switching-signal generator. L limiters, D frequency divider, S triangular-pulse generator. Wave forms in broken lines: without limiting; fully drawn: with limiting. The output terminals 1, 2 and 3 are connected to the switching-signal inputs s_1 , s_2 and s_3 of the electronic switches.

The resistors R_1 and R_2 are of equal value, and so the output terminals receive equally large alternating voltages of opposite polarity with respect to earth. These voltages are applied via blocking capacitors to the input of the push-pull amplifier for the beam deflection of the cathode-ray tube. Apart from the fact that the two voltages in anti-phase thus obtained are suitable for feeding the push-pull amplifiers, the cathode resistance gives a heavy negative feedback highly stabilizing the gain of the valves T_1 . This is necessary because in this part of the circuit the signals that are to be compared are transmitted by different valves and any variations of the gain of this stage would upset the accuracy of the calibration.

Switching-signal generator

As already mentioned when dealing with the principle of the system, the switching-signal generator supplies three different signals consisting

which would immediately be noticed, and a photograph would show thick lines unfavourably affecting the accuracy of the measurements.

The switching signals are generated in different stages, which will be explained with the aid of fig. 7.

A sinusoidal alternating voltage of 50 c/s is applied to a limiter L_1 , and to a frequency divider D . The latter passes every $1/25$ th of a second a pulse to a circuit S generating a triangular voltage with a frequency of 25 c/s. This triangular voltage is applied, in anti-phase, to two limiters L_2 and L_2' , which clip pieces out of the triangular voltages and thus produce square-wave pulses of the form shown in fig. 7. To these pulses are added the signals coming from the limiter L_1 . When the differences between the maximum and the minimum output voltages of L_1 and L_2 (or L_2') are equal then L_3 and L_3' receive pulses of the form drawn in fig. 7. From these signals, which have a repetition

reduced to zero it was found necessary to give the screen grid a negative potential with respect to the cathode.



Fig. 11. Double step-voltage generator for tracing the lattice lines. Immediately behind the panel are the two sets of 12 valves of the two second stages. On the right, in two rows of six, the valves of the common first stage.

Fig. 11 is a photograph of the step-voltage generator for tracing the lattice. The circuits are duplicated so as to allow the intervals between the horizontal and the vertical lines to be adjusted independently of each other. The valves of the first stage (T_1 in fig. 10) are common to both systems, but those of the second stage are separated. For adjusting the intervals there are two sets of 12 controls, seen in fig. 4 on the right-hand panel at the top. The two controls underneath these are for adjusting the amplitudes of the two step-voltage generators, this being done without altering the proportions of the steps.

The construction of the step-voltage generator supplying the grid voltages for the valve under test (V_g in fig. 1) is similar to that of the generator supplying the signals for tracing the lattice lines. The controls for this generator are seen in fig. 4 on the left-hand panel.

Deflection amplifiers

These are designed as normal A.C. push-pull amplifiers that have to reproduce frequencies, undistorted in amplitude and phase, in a range from 25 c/s (the picture frequency) up to about 50,000 c/s (the frequency of the higher harmonics of the step-voltage generators). The valve capacitances, and stray capacitances in the output circuit, form the limiting factors, but these are compensated by means of capacitors. The usual method of reducing the influence of stray capacitances, by employing small anode resistances, could not be used here for the following reason. The output voltages required for the deflection plates of the cathode-ray tube have to be high (about 300 volts), so that if small anode resistors were used the output valves would have to deliver high powers which would be needlessly dissipated in the resistors.

By means of a compensating circuit such as used by Carpentier⁴) it has been possible to use anode resistors of a high value (100,000 ohms) and amplifying valves (type CF. 50) which are capable of supplying high alternating voltages with only a small amount of distortion. The gain is constant between 10 and 15,000 c/s within $\pm 2\%$ (between 10 and 60,000 c/s it is constant within $\pm 20\%$); the phase shift is less than $\pm 2^\circ$ between 10 and 15,000 c/s.

With a push-pull amplifier the compensation can easily be obtained by coupling the grids of the amplifying valves in one of the stages, via a small capacitance C_c , to the anodes of the corresponding valves of the other phase, as is done in neutralization. The only difference is that in the case of normal neutralization only the anode-to-grid capacitance is rendered harmless, whereas here an additional voltage 90° in advance of the signal is applied to the grid via the capacitor C_c . Thus the anode current is increased by the charging current of the anode capacitance.

For a flat frequency characteristic the capacitance C_c of the compensating capacitor has to bear a certain relationship to the grid capacitance plus the stray capacitance (sum C_0), such that the condition $C_0/C_c = R_g S$ is satisfied; here R_g represents the equivalent resistance of the anode resistance of the valve in the preceding amplifying stage and the grid-leak resistance of the valve in the last stage connected in parallel, whilst S is the mutual conductance of the latter valve.

⁴) E. E. Carpentier, A cathode-ray oscillograph with two push-pull amplifiers, Philips Techn. Rev. 9, 202-210, 1947.

In our case $R_g = 25,000$ ohms, $S = 5$ mA/V, $C_0 = 300$ pF, so that C_c has to be given a value of about 3 pF.

The compensating capacitances have been obtained with the aid of trimmers in series with a fixed capacitor of 3.3 pF.

With this system it has to be borne in mind that both the valve capacitances and stray capacitances, as well as the compensating capacitances additionally load the output stage, which at high frequencies involves an increase of the A.C. output current. It is therefore advisable to keep the stray capacitances as small as possible by careful assembly.

Supply units

For the proper functioning of the diagram tracer, direct-current sources of highly constant voltages are essential. Not only must the voltage be independent of the mains voltage and frequency, but it also has to be free of ripple and hum. Furthermore, the sources have to be variable within a wide range and have a small internal impedance.

The supply units used are in principle similar to those described in this journal in 1941⁵⁾. There the mains-independent voltage was obtained by balancing the output voltage against the reference voltage from a dry-cell battery; the potential difference between the two voltages influences the resistance of a regulating valve incorporated in the current circuit in such a way that the output voltage remains practically constant. In the apparatus used here the dry-cell batteries are replaced by separate voltage sources kept constant with neon voltage-reference tubes. For the functioning of the regulating valve a pentode is used instead of a triode. Since a high degree of stabilization requires a high amplification factor in the regulating valve, with a pentode a better regulation is obtained, whilst at the same time the hum ripple is suppressed to less than 1 mV. (For details see the article quoted in footnote⁵⁾.) With this construction of the supply units a variation of 5% in the mains voltage causes a variation of only 0.01% in the output voltage.

For the supply of the deflection amplifiers, however, the hum level is still too high. To reduce this further, a very large smoothing capacitance would be required. With the aid of a so-called reactance valve⁶⁾ this can be achieved with a comparatively small capacitor. With suitably chosen elements the valve is equivalent to a capacitance

of RS times the capacitance in the grid circuit, where R is the value of a resistor connected in series with this capacitance in the grid circuit and S is the effective mutual conductance of the reactance valve. By using a pentode, a factor $RS = 1800$ was reached.

For the anode supply of the valve under test, in addition to a direct-voltage source V_a (fig. 1) an alternating-voltage generator G is also required for the periodical variation of the anode voltage. The generator consists of an R - C generator followed by a push-pull power amplifier with an output of 200 W, this being necessary for measuring output valves. The frequency can be varied between 700 and 1800 c/s, and is asynchronous with the mains frequency, so that the transitions from one curve to the next (at the change of the grid voltage taking place synchronously with the mains frequency) are distributed over the screen of the cathode-ray tube, leaving no visible connecting lines between them.

The R - C generator consists of a two-stage amplifier fed back by a network of resistances and capacitances. The circuit starts to oscillate at the frequency at which the input voltage of the network is in phase with the output voltage⁷⁾.

The sine-wave voltage generated in this way is applied to an amplifier the output stage of which is formed by a push-pull amplifier with 2×2 valves, type EL 34, connected in parallel. At an output of 200 W the maximum amplitude is about 220 volts. The maximum variation obtainable in the anode voltage is therefore $2 \cdot 220 / 2 = 620$ V. As indicated in the block diagram of fig. 1,

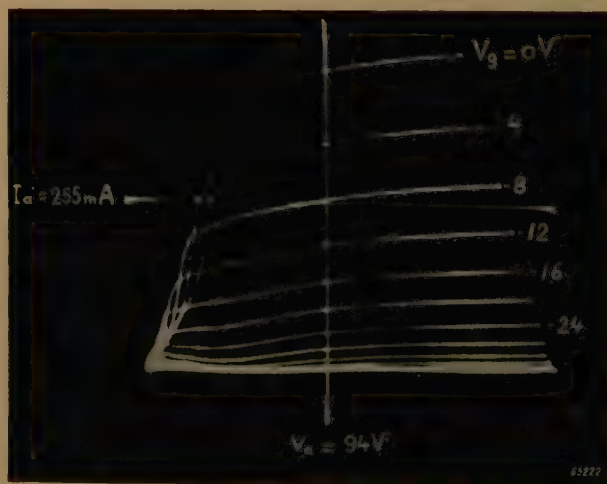


Fig. 12. Electronic crosshair on the I_a - V_a characteristics of a television pentode PL 81.

⁵⁾ H. J. Lindenhovius and H. Rinia, A direct-current supply apparatus with stabilised voltage, Philips Techn. Rev. 6, 54-61, 1941.

⁶⁾ See, e.g., Philips Techn. Rev. 8, 47, 1946.

⁷⁾ See, e.g., J. J. Zaalberg van Zelst, Stabilised amplifiers, Philips Techn. Rev. 9, 24-32, 1947.

in series with this generator is a direct voltage source. The two voltages can be adjusted individually, so that any anode-voltage range can be examined.

Calibration of the lattice

For calibrating the lattice the valve under test (T in fig. 1) is disconnected, and the resistor R in fig. 1, shunted across the input b_2 of the electronic switch V (fig. 2), is connected to a variable current source fitted with a milliammeter.

The voltage divider, connected to the input b_2 of the electronic switch H (fig. 2), is connected to an adjustable direct-voltage source with a voltmeter. Instead of a set of curves being traced a fluorescent spot is seen on the screen of the cathode-ray tube. With this spot, the coordinates

of which are exactly known, the lattice is calibrated in the following way.

First the current and voltage sources are switched off. The spot then indicates on the screen the position of the origin of the system of coordinates. The origin of the lattice has to coincide with this point, any adjustments needed being made with the potentiometers R_4 (fig. 6) of the electronic switches.

The current and voltage of the calibrating point are then adjusted to the values corresponding to the first horizontal and vertical lattice lines to be traced. The point where these lines intersect has to coincide with the calibrating point, adjustments being made with the potentiometers R_3 (fig. 10). In this way all the lattice lines are adjusted in succession.

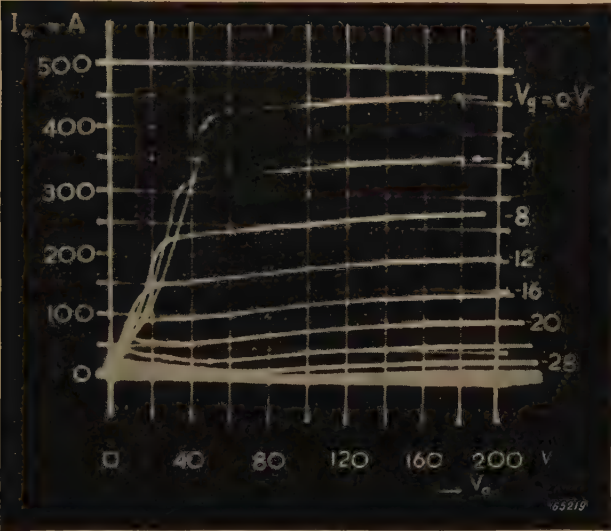


Fig. 13. I_a - V_a characteristics of a television pentode PL 81 (line-output pentode). Screen-grid voltage 180 V.

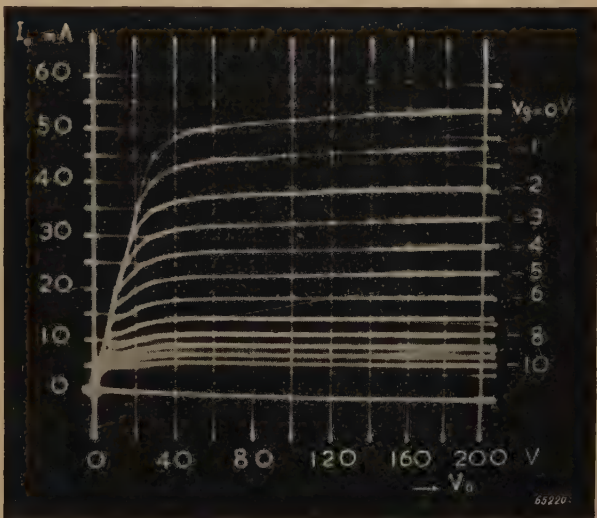


Fig. 14. I_a - V_a characteristics of the pentode part of a triode-pentode ECL 80. Screen-grid voltage 170 V.

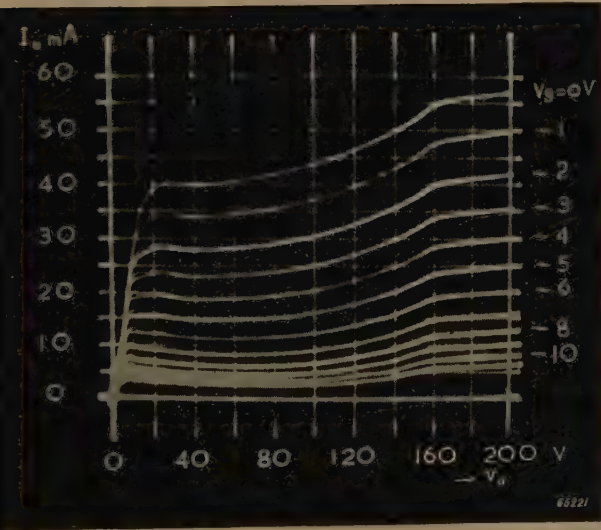


Fig. 15. As in fig. 14, but with the third grid and anode interconnected.

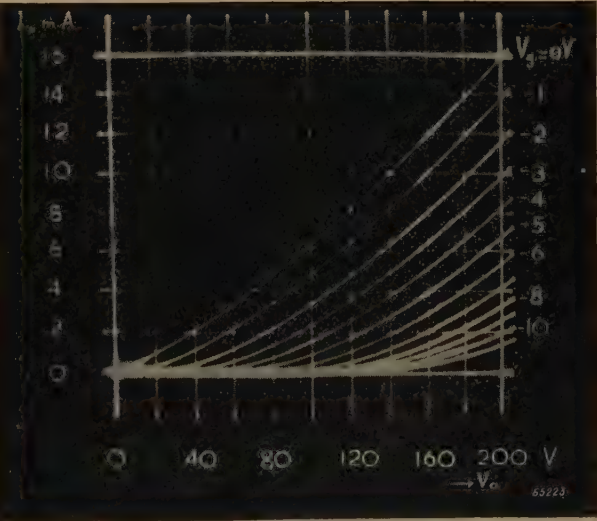


Fig. 16. I_a - V_a characteristic of the triode part of an ECL 80.

Usually the lattice will be so adjusted that the distance between two successive lines corresponds to equal potential differences at the terminal b_2 .

As a rule it will be found that the voltage steps at the output of the step-voltage generator are not exactly equal, owing to the curvature of the characteristic of the operative valve of the electronic switch. Neither will the lattice lines on the screen of the cathode-ray tube then be equi-distant, because the deflection of the cathode-ray tube will not be exactly linear with the voltage on the deflection plates. However, owing to the method of calibrating described, no errors arise from these two discrepancies.

Electronic crosshair

To determine the coordinates of an interesting point, as for instance a bend or maximum in a characteristic, without interpolation between two lattice lines, the apparatus is provided with an "electronic crosshair" which can be moved across the screen. For this purpose the step-voltage generator can be replaced by variable direct-voltage sources the voltages of which can be measured with two moving-coil meters. Instead of the lattice there then appear on the screen of the cathode-ray tube two coordinate lines the values of which are known from the readings of the moving-coil meters. These meters are mounted on the panel immediately above the cathode-ray tube (fig. 4).

This method of determining the coordinates with the aid of the crosshair is less exact than the lattice method, because errors may arise from the inequality of the operative valves of the electronic

switches. The crosshair method is nevertheless useful when it is desired to determine the coordinates of a point visually, for the errors due to the cause mentioned are less than those resulting from interpolation by eye between two lattice lines. Moreover, when greater accuracy is desired, there is a possibility of calibrating the coordinates of the intersecting lines, after adjustment, with the method applied for the lattice.

Fig. 12 is a photographic recording of the screen picture with electronic crosshair. Figures 13, 14, 15 and 16 are photographs of the lattices and characteristic curves of television receiving valves, reproduced here to give an idea of the quality of the diagrams.

Summary. An apparatus is described with which a series of curves, e.g. the I_a - V_a characteristics of an electronic valve, and a calibrated lattice of coordinates can be traced simultaneously on the screen of a cathode-ray tube. In cycles of 1/25th of a sec the spot traces in succession the vertical lines of the lattice, the family of curves being examined, the horizontal lines of the lattice and once more the family of curves. The pairs of signals for tracing these three pictures are applied to the cathode-ray tube by means of two electronic switches. The lattice is calibrated by replacing the electrical quantities to be measured by two known direct voltages which are adjusted so that the spot coincides with a chosen point on the lattice. In this way the influence of non-linearities in the apparatus is eliminated. The diagrams produced can be measured with an accuracy of 1% on photographic recordings. The coordinates of any point can be exactly determined with the aid of an "electronic crosshair", which can be moved across the screen of the cathode-ray tube by the adjustment of two direct voltages.

APPLYING COATINGS BY ELECTROPHORESIS

by S. A. TROELSTRA.

621.359.3:537.363

Coating by electrophoresis, whereby very small suspended particles are deposited on an electrode with the aid of an electrostatic field, is a process that has been known for a long time. The mechanism of this process has been better understood since a deeper insight has been obtained in regard to the phenomena determining the general behaviour of suspensions. By employing organic media it has been possible to develop electrophoresis into a technically useful method, which is now being applied on a wide scale in the manufacture, for instance, of radio valves.

The investigations which have led to this and which were carried out by Verwey, Hamaker and others in the Philips Laboratory at Eindhoven, were initiated by Prof. Dr. J. H. de Boer, formerly also of this laboratory.

The principle of electrophoretic coating is easily demonstrated with the following experiment. Two electrodes are immersed in a vessel containing a rather concentrated suspension of ground soapstone (a natural magnesium silicate) in alcohol. As electrodes, graphite or some metal not readily corroding electrochemically is chosen. After applying a direct voltage of some hundreds of volts for a few seconds and then lifting the electrodes out of the suspension, it is seen that in that short space of time the anode has been covered with a layer of soapstone about 1 mm thick, whereas the cathode is still bare. When the experiment is immediately repeated with the voltage reversed in polarity it is found that the deposit on the anode has completely or partly disappeared and that the other electrode is then coated. Provided the suspension is well stirred from time to time, this process can be repeated many times. The photograph in *fig. 1*

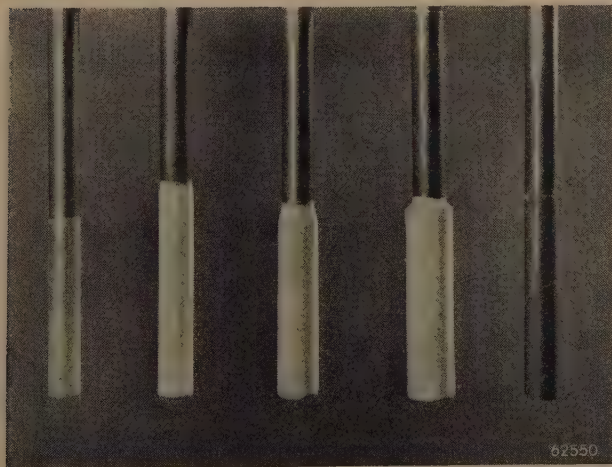


Fig. 1. Graphite electrode coated with soapstone by electrophoresis. Extreme left: after immersion only. To the right of this: after current has passed through the bath for 1, 3 and 10 seconds respectively. Extreme right: the electrode on which a deposit had been formed during 3 seconds and then removed by passing current through the bath in the opposite direction during 1 second.



Fig. 2. The settling of a suspension of quartz in water. From left to right: after 5 seconds, 10 hours and 2 weeks respectively.

shows the coating of a graphite electrode at different stages.

This process, by means of which also insulating substances can be deposited, resembles very much that of electro-plating, where metals are deposited on the cathode electrolytically. In both cases the material to be deposited apparently migrates under the influence of the electric field, and this would indicate that the particles in the suspension are electrically charged.

The deposit formed on the electrode has very much the appearance of the sediment which after some time settles out of a suspension on the bottom of the vessel. *Fig. 2* shows what happens when, after thorough shaking, a suspension of ground quartz powder (particle diameter about 1-10 μ) in water is left to stand. The liquid gradually clears from the top downwards, but not with any sharply defined demarcation because the rate at which the particles settle differs according to their grain size. The liquid in the lower part of the vessel is

denser and the layer of sediment on the bottom gradually increases in thickness. After some time there is a firm sediment, and when this is thoroughly stirred up or the vessel is well shaken we again get the suspension in its original state.

When the quartz powder is suspended in toluene instead of in water the result is entirely different. Then, after shaking, the powder settles rapidly in the form of cohering flakes (see *fig. 3*). A clear top layer is very quickly formed, with a sharp demarcation, the interface then gradually sinking lower until at last it practically comes to rest. The precipitate shows much less cohesion than in the former



Fig. 3. The settling of a suspension of quartz in toluene. From left to right: after 5 seconds, 10 hours and 2 weeks respectively. In this unstable suspension the particles flocculate immediately and the liquid clears after a short time. Note the "buttermilk effect" on the inside of the flask.

case and with the slightest movement of the vessel tends to rise again. Furthermore, the flakes formed in the liquid cannot be entirely dispersed again even by thorough shaking, so that the original fine distribution of the powder can never be realized in this medium. In this case one speaks of an unstable suspension, as compared with a stable suspension in the former case.

Under certain conditions, about which more will be said later, also in the case of electrophoresis it may happen that the deposit shows little cohesion, so that much of the coating comes away from the electrode in thick lumps. In essence the formation of a coating by electrophoresis takes place in the same way as the sedimentation under the influence of gravity in the experiments just described. For a good understanding of what takes place in electrophoresis it is therefore of interest first to investigate the properties of suspensions in general.

Stability of suspensions

Suspensions may be stable or unstable. Let us first discuss this difference. Phenomena of stability and instability have long been known in colloidal chemistry and extensively studied with systems of particles that are microscopically indiscernable.

There is no fundamental difference between these colloidal dispersions (sols) and suspensions, and no sharp line can be drawn between the two. The main point of difference lies in the size of the particles forming the dispersed phase. For sol particles a diameter of 0.1μ is to be taken as a maximum, whilst in a suspension about $1\text{--}\mu$ is the minimum. Owing to this difference in size the particles in a suspension settle fairly quickly, within a few hours. In the case of sols, however, it may take days for the particles to settle, and if they are small enough they may scarcely settle at all. In fact this applies only for stable systems in which there is no mutual adhesion of the particles. In the case of an unstable system there is adhesion; aggregates (floculates) are formed which settle much quicker than the original particles. From the rate of sedimentation alone it cannot therefore be seen whether one has separate particles or floculates of finer particles, while account has also to be taken of the fact that the rate of sedimentation is further dependent upon the specific gravity of the settling units.

Consequently, in order to decide whether a given system is stable or unstable it is necessary to consider not only the rate of sedimentation but also other properties in which these systems differ. Here we would only mention the firmness and the volume of the sediment and the manner in which the suspension runs down a wall (the marks left on the inside of a bottle of buttermilk after it has been emptied are typical for a "floculated" suspension).

The properties of suspensions can be explained by the assumption that there is an electric double layer around the particles. First it will be shown how this may arise and then how the stability can be accounted for by the forces due to that layer.

How the double layer is formed

Extensive investigations have confirmed that as a rule the surface of the dispersed particles is electrically charged, such in contrast to the inside of the particle, which may either be built up from neutral molecules or formed into a neutral whole by the interchange of positive and negative elements¹).

¹) See, e.g., J. Alexander, *Colloid Chemistry*, Reinhold, New York 1931; H. R. Kruyt and others, *Colloid Science I*, Elsevier Publishing Co., Amsterdam (at press).

In the interface it is possible for various processes to take place which cause the surface to be charged. Of the charged elements just mentioned — which also occur in a small concentration in the liquid when the solution is in equilibrium — one kind may be more strongly bound than the other. Or else ions may be formed through reaction of the surface of the original particles with the medium. And finally it is possible for foreign ions, purposely added or not, to be bound.

The surface charge, no matter how it arises, is accompanied by an equivalent but opposite charge in the liquid, in the shape of a number of mobile ions which are simultaneously subjected to the electrical attraction of their partners on the wall and to a thermal diffusion which tends to distribute them uniformly in the liquid.

The sum total of these influences is that the particle is surrounded by an "atmosphere" of counterions, usually referred to as a "cloud", in which the density of the charge diminishes outwards. Together with the surface charge these ions form the electric double layer previously mentioned.

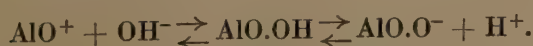
A condition for the formation of the double layer is, therefore, that the liquid must have a more or less ionizing action, though it is by no means essential that the material of the particle itself should be subject to ionization.

The chemical nature of the material will usually be reflected in the structure of the double layer. Quartz (SiO_2) in water, for instance, will form on the surface silicic acid (H_2SiO_3), which dissociates according to the formula $\text{H}_2\text{SiO}_3 \rightleftharpoons \text{SiO}_3^{--} + 2\text{H}^+$, whereby the two H^+ ions pass over into the medium and the SiO_3^{--} ion is left on the surface. The other possibility of dissociation: $\text{SiO}(\text{OH})_2 \rightleftharpoons \text{SiO}^{++} + 2\text{OH}^-$, is only found in very strongly acid surroundings (low OH concentration), so that it may be said that quartz has a decidedly negative character.

Rutile (TiO_2) is more amphoteric in nature, so that a trace of acid is already sufficient to give the surface a positive charge, such in accordance with the formula: $\text{H}_2\text{TiO}_3 \rightleftharpoons \text{TiO}^{++} + 2\text{OH}^-$.

Zirconia (ZrO_2) has an even greater tendency to a positive charge than rutile, though here too a trace of acid in the medium is desired.

As further examples may be mentioned Al_2O_3 and Fe_2O_3 . The first of these is decidedly amphoteric: with water as medium, in the surface $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O} = 2\text{AlO.OH}$ may be formed, the dissociation of which may take place in two ways, viz:



Iron oxide (Fe_2O_3) is more positive and thus disso-

ciates according to the formula $\text{FeO.OH} \approx \text{FeO}^- + \text{OH}^-$. Under certain conditions, e.g. at a certain p_{H} , in suspension an amphoteric substance will have just as many positive as negative ions (or groups of ions) in the surface and thus, in the sum, it will not be charged. It is then said that the point of zero-charge or the isoelectric point is reached.

Thus it is seen that the nature of the medium will as a rule greatly influence the quantity and distribution of the ions, so that even the sign of the charge may differ. In toluene for instance there is extremely little ionization of quartz, so that there is but little development of the double layer. Finally it is pointed out that in the case of very weakly polarized substances it is often necessary to provide for a sufficient surface charge by adding highly adsorbable ions. For electrophoretic coating one mostly uses alcohols or ketones as suspension media. It is true that these liquids have a much less dissociating action than water, but on the whole the same views hold ²⁾.

Explanation of stability

When two suspended, charged particles approach each other the counter-ion clouds infiltrate one through the other and change in character. It is not easily seen whether the particles then attract or repel each other, but with the aid of a detailed theory Verwey and Overbeek ³⁾ have shown that a repulsion takes place, whereby, in the case of spherical particles for instance, the potential energy of the particles decreases roughly exponentially with their distance.

The order of the repulsion is further influenced by the size of the particles and the electrolyte content of the medium.

In addition to the repelling force determined by the structure of the double layer, however, there is also an attractive force taking part, viz. the Van der Waals-London attraction. This arises from the fluctuating distribution of the charge in atoms (also in neutral ones) and the accompanying induction of dipoles in neighbouring atoms. The corresponding attraction energy Φ_a can be represented, for not too great a distance r between two atoms (molecules), by $\Phi_a = \lambda/r^6$, where λ is a constant the value of which depends upon the properties of these atoms (molecules). When one has to do with groups of atoms or molecules the attraction energy is also influenced by the shape and size of the particles and diminishes somewhat less

²⁾ E. J. W. Verwey, Properties of suspensions, especially in non-aqueous media, *Rec. Trav. chim. Pays Bas* **60**, 618-624, 1941; The electrical double layer of oxidic substances especially in non-aqueous media, *ibidem* 625-633.

³⁾ E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the stability of lyophobic colloids*, Elsevier Publishing Co., Amsterdam 1948.

rapidly with the distance from the surface of the particles.

Finally, at the very smallest distances, thus when the atoms touch each other, there is always repulsion due to the mutual penetration of the orbits of the electrons.

When both attractive and repelling forces are concerned these have to be combined to find the resultant effect ⁴). From the foregoing it follows that for small distances attraction will prevail in most cases. Only exceptionally will conditions be such that repulsion predominates at any distance between two particles. The latter case is illustrated by curve *a* in *fig. 4*, where the potential energy has been plotted against the distance *r*; here we certainly have a stable suspension.

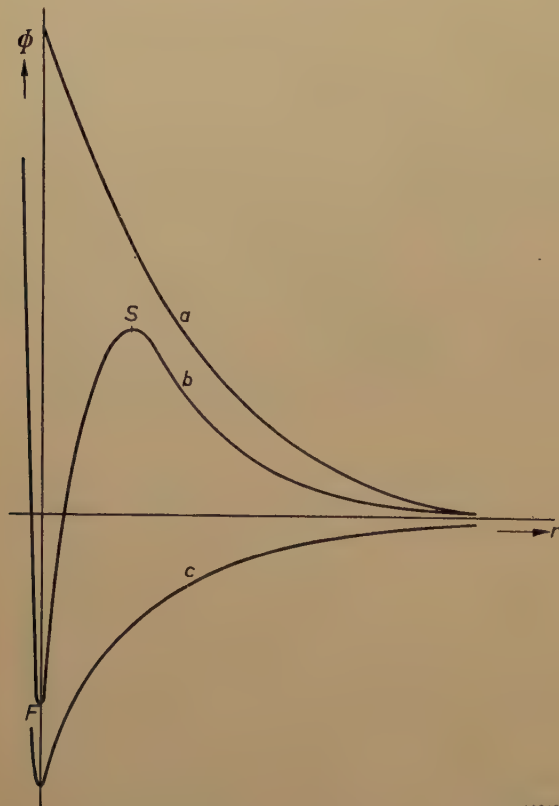


Fig. 4. Variation of the potential energy as a function of the distance between two particles,
a) for a stable suspension,
b) for a suspension which is unstable for short distances between the particles (greater concentration),
c) for an unstable suspension.

When, however, the force of repulsion is small (curve *c*) coagulation takes place spontaneously and the system is thus unstable. It is interesting to note the apparently general case that repulsion

occurs at great distances and attraction at small distances; the curve *b* then shows a maximum (*S*), an "energy threshold", that has to be overcome by the partners before adhesion is possible. Thus the system then has some degree of stability according to the height of the maximum, but any incidental forces, purposely introduced or not, may cause the particles to move to the minimum (*F*) of the potential energy.

When the medium is changed, for instance by choosing a different solvent or adding or extracting some electrolyte, it is possible that the energy curve becomes transposed from the one type to the other, so that the stability likewise changes in character.

Turning back for a moment to our examples, the system of quartz in water can be described by a curve of the type *b* (*fig. 4*), and that of quartz in toluene by a curve of the type *c*. If ionization at the surface of the quartz is promoted by adding a little NaOH to the water, then perhaps a curve of the type *a* can be reached. It appears that in the lower alcohols and ketones there is sufficient ionization to reach an energy curve of the type *b* or even *a*.

Sedimentation in suspensions

With this rough insight into the essence of stability it is not difficult to understand why it is just a stable suspension which, under the influence of gravity, yields a dense, compact sediment: in such a stable system the particles settle separately, and those which settle most readily will temporarily stay in suspension at a distance where their weight balances with the repelling forces opposing any closer approach. (Here it is assumed that the bottom has the same sign of charge as that of the particles, and that for the interaction between particle and bottom approximately the same conditions hold as between two particles.)

The weight of the particle implies the presence of a third force, which in the energy diagram may be represented by a straight line drawn through the origin; with this as well as with the other lines the slope is a measure of the force applied ⁵). As more particles settle and (via the repelling forces) bring their weight to bear upon the underlying particles this third force is increased and thus the slope of the straight line assumes a larger angle. The consequences of this are evident when we add up the original and the last energy curves. In *fig. 5* a curve is given of the type *b* corrected with a gravity term for a number of pressures directly related to the height of the sediment. It is seen that as the

⁴) H. C. Hamaker, A general theory of lyophobic colloids, *Rec. Trav. chim. Pays Bas* **55**, 1015-1026, 1936; and **56**, 3-25, 1937; A system of colloid phenomena, *Rec. Trav. chim. Pays-Bas* **56**, 727-747, 1937.

⁵) H. C. Hamaker, The influence of particle size on the physical behaviour of colloid systems, *Trans. Faraday Soc.* **36**, 186-192, 1940.

thickness of the layer increases so the original curve is tilted upward more and more. The distance r_M from the ordinate to the minimum M is apparently, under these conditions, the average distance of

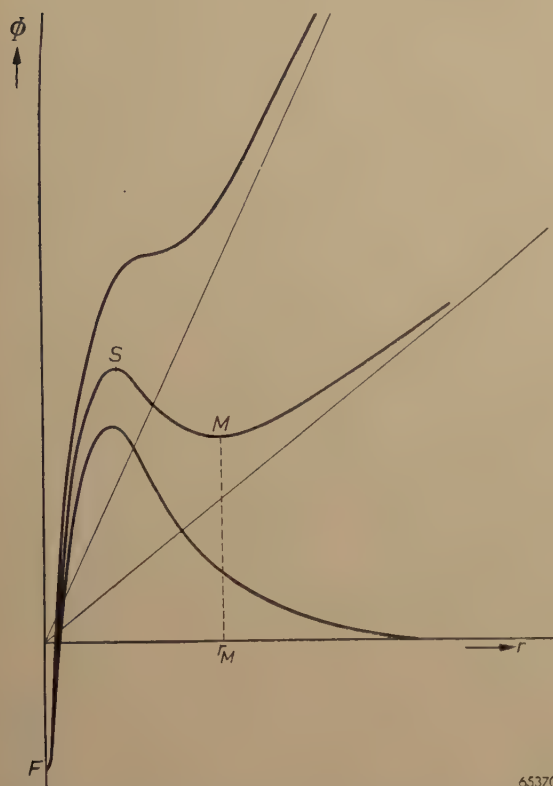


Fig. 5. As in fig. 4b, where account is taken of compression due to the force of gravity. The steeper the curves, the closer the minimum M and the maximum S come together and the more readily an aggregate is formed.

the particles. The difference between the maximum S and the minimum M gradually diminishes until they both disappear simultaneously. But before this situation is reached the difference $S-M$ will have become so small that, owing to thermal motion, the particles will be propelled one after the other from M beyond S and finally reach the energy minimum F ; not until then is adhesion possible. Summing up, it may be said that in a stable suspension of the type b first a concentrated suspension is formed near the bottom of the vessel and that this suspension gradually increases in concentration but diminishes in stability, until, starting from the bottom, the particles reach the state of coagulation.

The original curve b can be restored by eliminating the field of gravity — by tilting up the container — but as a rule it is not possible to separate in this way the particles that have already clung together; for this greater forces are needed, such as may be brought about by shaking or vibrating.

In the case of a sediment formed from a suspension of the type a , tilting of the container will

indeed cause a mutual displacement of the particles: the layer is caused to flow, though often very slowly, and the particles gradually move farther apart. Fig. 6 gives for this case the family of curves analogous to fig. 4a.

If, on the other hand, the sediment is formed from an unstable suspension (type c) then a very rare structure with little cohesion is obtained. In a stable suspension the particles had an opportunity, right up to the last moment, to unite into a very compact structure, the double layers having prevented direct contact of the particles and having made it possible for them to shear along each other; thus the double layers act as a sort of lubricant. In the case of an unstable suspension, on the other hand, partial aggregation attended by flocculation takes place already before sedimentation is completed.

Before proceeding to make a comparison between a sedimentated layer and one obtained electrophoretically we have to consider the process of electrophoresis itself.

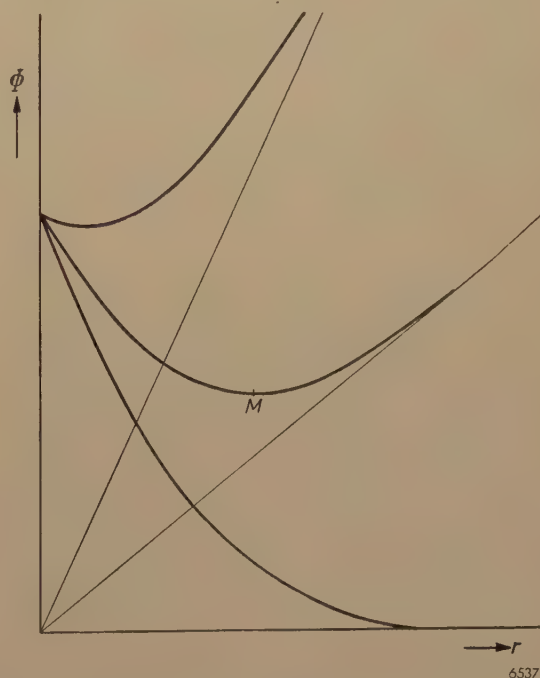


Fig. 6. As in fig. 4a, but taking into account the force of gravity.

Electrophoresis

Electrophoresis — the transportation of a particle in a colloidal solution or in a suspension under the influence of an electric field — has been known for a long time; in fact it yielded one of the first indications of the state of charge of colloidal particles. At first sight it seems to be a simple process: the electric force K exercised upon the charge q by the

field F can be imagined as being compensated by the friction to which the particle is subjected in the medium and which, according to a formula given by Stokes for a spherical particle, amounts to $6\pi\eta av$ (η = viscosity of the medium, v the velocity and a the radius of the particle), thus being proportional to the velocity. Hence the following formula may be written:

$$K = qF = 6\pi\eta av, \text{ or } v = \frac{qF}{6\pi\eta a}. \quad (1)$$

In reality the theory of electrophoresis is much more complicated than this, because, owing to the friction of the liquid carried along with them, the counter-ions moving in the opposite direction exercise a retarding action upon the particle; further, the cloud of counter-ions itself is distorted and, moreover, a thin layer of liquid is also carried along with the particle⁶⁾.

The potential at the boundary of this liquid sheath reckoned with respect to a point in the medium at a remote distance from the particle (called the electrokinetic potential ζ), which naturally depends greatly upon the surface charge and the structure of the counter-ion cloud, has proved to be a very useful quantity for theoretical considerations, in addition to the ratio of the radius of the particle and the "thickness" of the double layer.

Calculations yield the following formula for the mobility u of a spherical particle in the suspension:

$$u = \frac{v}{F} = \frac{\varepsilon\zeta}{6\pi\eta} \cdot f(\kappa a, \zeta),$$

where ε represents the dielectric constant of the medium and π is a quantity known from the theory of electrolytes. $1/\kappa$ corresponds fairly well to the effective "thickness" of the double layer, i.e. the distance from the surface at which, for the sake of simplicity, any diffuse counter-ion charge can be imagined as being concentrated in one plane.

For large particles, as in our suspensions, the function $f(\kappa a, \zeta)$ assumes the value of 1.5, so that we may write:

$$u = \frac{\varepsilon\zeta}{4\pi\eta}.$$

With the aid of simplifying assumptions it is possible to derive from this a formula of the type (1), viz:

$$u = \frac{q}{4\pi\eta a(1 + \kappa a)}.$$

By way of orientation it may be said that the value of a will usually lie between 10^{-4} and 10^{-3} cm and that of κ between 10^4 and 10^6 cm⁻¹, so that the velocity is often much smaller than the value that would follow from equation (1).

Now, when a potential difference is applied between two electrodes immersed in a suspension, a current begins to flow through that suspension and the suspended particles migrate towards one of the electrodes (which one depends upon the sign of the charge; to define our thoughts it will be assumed that q is negative and thus that the particles migrate towards the anode).

Electrophoretic coating

Having explained in detail the formation of a sediment under the influence of a gravitational field, we can be brief in dealing with the deposition of a coating by electrophoresis. The mechanism of the process is on the same lines, except that the motive force is of an electric nature⁷⁾. The same curves as those given in figs 5 and 6 apply for the variation of the potential energy, but curve b will be considered more closely in a quantitative sense.

In fig. 7 the potential energy of two small spheres has been plotted against the distance between their

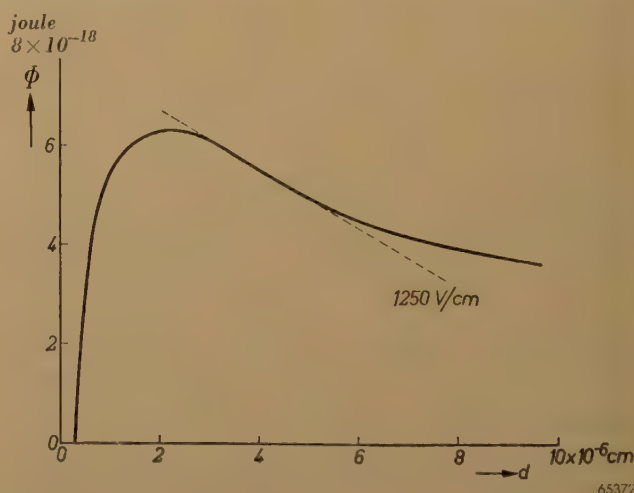


Fig. 7. Potential energy of two small spheres with surface charge and ion cloud, as a function of the distance d between their surfaces. For the numerical calculation the values taken are: $\varepsilon = 26 \varepsilon_0$ F/m⁸⁾ (acetone), $\zeta = 100$ mV, $a = 10^{-4}$ cm, $\kappa = 10^5$ cm⁻¹, whilst a plausible value has been given to the Van der Waals-London constant.

⁷⁾ J. H. de Boer, H. C. Hamaker and E. F. W. Verwey, Electro-deposition of a thin layer of powdered substances, Rec. Trav. chim. Pays Bas **58**, 662-665, 1939.

H. C. Hamaker and E. F. W. Verwey, The role of the forces between particles in electro-deposition and other phenomena, Trans. Faraday Soc. **36**, 180-185, 1940.

⁸⁾ Here units of the rationalised Giorgi system are used. ε_0 , the dielectric constant in vacuo, amounts to $10^7/4\pi c^2 = 0.885 \cdot 10^{-12}$ F/m, where c represents the velocity of light in vacuo.

⁶⁾ J. Th. G. Overbeek, Advances in Colloid Science III, 97-135, New York 1950.

surfaces. The constants determining repulsion and attraction have been given plausible values, which lead to a curve of the type of fig. 4b. It is observed that to the right of the maximum the slope of the energy curve indicates the magnitude of the repelling force exercised by one particle upon another, thus also the magnitude of the force which is just sufficient to prevent the particles from moving apart.

The slope in the bending point of the curve is proportional to the minimum force required to drag the particle up against the "energy crest". The field strength F needed for this proves to be 1250 V/cm. The question arises whether it is possible to produce this relatively high field strength.

In principle, of course, this is always possible by raising the voltage between the electrodes. A high field strength can also be obtained locally, however, with a relatively small potential difference, namely in the vicinity of a cylindrical electrode of small diameter.

We shall now calculate the field for an arrangement with two coaxial, cylindrical electrodes. Ignoring boundary effects, it may be assumed that the field is dependent only upon the distance r to the axis of the cylinders and that it does not change in the direction parallel to the axis. Denoting the specific conductivity of the suspension by γ and the height of the cylinder by l , the current I passing along a cylinder at the distance r from its axis is given by

$$I = 2\pi r l \gamma F \quad (2)$$

In a homogeneous suspension the value of γ is the same everywhere, so that apparently F is inversely proportional to r .

By integration we find the potential E as function of the distance r to the axis as:

$$E = \int_{R_1}^r F dr = \frac{I}{2\pi l \gamma} \log_e \frac{r}{R_1} \quad (3)$$

where R_1 represents the radius of the inner electrode.

In fig. 8 the potential and the field strength have been plotted for a potential difference of 200 volts between cylindrical electrodes with radii of 0.05 and 1.25 cm. With these dimensions the field strength at the surface of the inner electrode appears to be 1240 V/cm.

This is thus the potential variation when the conductivity γ has the same value everywhere in the vessel.

The electrophoresis itself does not cause any local differences in concentration of the particles in the suspension, not even in a cylindrical arrangement, as one might at first sight be

inclined to suppose. Given that the concentration of the particles is c , then the number of them passing along a cylinder at a distance r from its axis is:

$$2\pi r l \cdot u F c \quad (4)$$

Now, according to equation (2), F was inversely proportional to r , whilst the mobility u has to be taken as being constant. Thus the number of particles passing along is independent of r and in a cylindrical shell there are just as many particles entering from the outside as there are emerging from the inside, so that there is no increase in the number of particles in the shell.

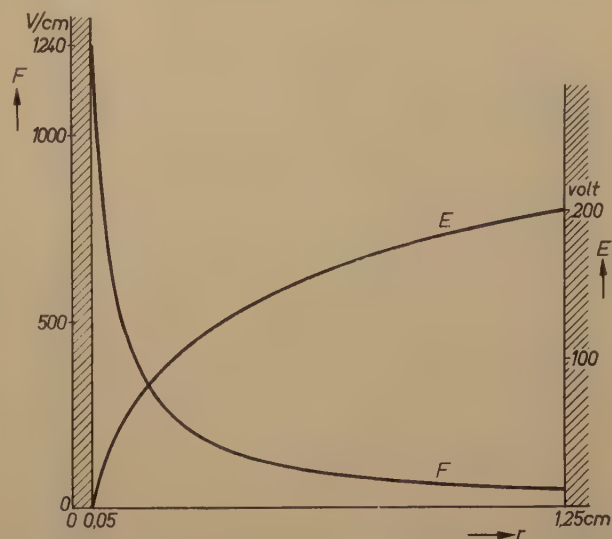


Fig. 8. Values of the potential E and the field strength F in the space between two coaxial cylinders, as functions of the distance r to the axis, at a voltage of 200 V between the cylinders.

Now in many cases it has been observed that, in spite of stirring, with a constant electrode voltage the current gradually decreases. Apparently, therefore, the deposited layer has a higher resistance than the suspension, and as a consequence the voltage drop within the deposit increases.

Curve 2 in fig. 9 gives the potential variation inside the vessel when assuming that around the inner electrode a layer has been formed in which the conductivity is five times smaller than that in the suspension.

There are indications that the resistance of the layer is not a simple dissipative resistance. Considering that, owing to the electric field, a change takes place in the counter-ion atmosphere around each particle, which amounts to a polarisation, it is not surprising that often a much lower resistance is found with alternating current than with direct current. All the factors related to the resistance are, however, by no means explained.

As is the case with sedimentation, the forces acting upon the particles in the layer are continually increasing, since the outermost layers bear upon the underlying ones. But with electrophoresis the

forces may also, in certain cases, be considerably increased by the gradually increasing field strength inside the layer.

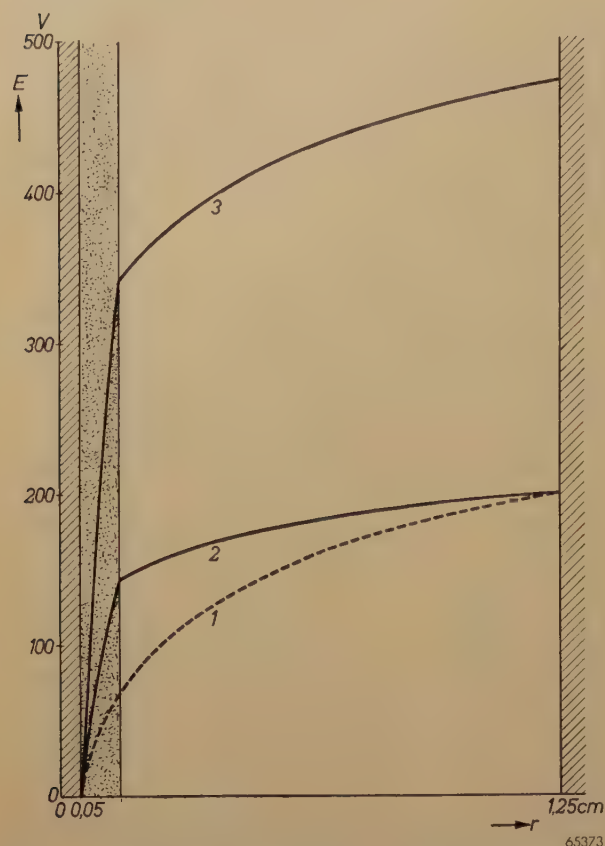


Fig. 9. Value of the potential E in a cylindrical arrangement for electrophoretic experiments. 1 when applying an electrode voltage of 200 volts; 2 when a layer 0.1 cm thick has been formed, while keeping the electrode voltage constant; 3 ditto when the current is kept constant and the voltage increases owing to greater resistance.

The electrophoretic yield

When a layer is being formed by means of electrophoresis the particles do not lose their charge upon being deposited on the electrode, just as is the case when the particles settle on the bottom of a vessel owing to the force of gravity. The process of deposition may be regarded as an accumulation of, for instance negative, particles on the electrode (anode), whereby the current transportation corresponding to their displacement (Kohlrausch's law) is brought about by secondary processes at the electrode. If the material of this electrode is not a precious metal like gold or platinum, e.g. of copper or nickel, then it yields new ions (Cu^{++} or Ni^{++}) which neutralize the supplied charge in the vicinity of the electrode. If the electrode is made of a precious metal or graphite then the ions (e.g. H^+) formed from the solvent take over this function, whilst their partners (OH^-) are discharged at the surface.

Thus it is just the same as in the case of the accumulation of sulphate ions (SO_4^{--}) in the electrolysis of a sulphate solution. On an anode of platinum a solution of sulphuric acid (H_2SO_4) is then formed. The only difference is that by the same process the particles in a suspension cake together into a layer like "giant ions", whilst the neutralizing charge — thus the counter-ion cloud — finds plenty of space between the particles. The "thickness" of the double layer may be of the order of 10^{-6} cm and the size of the particles 10^{-4} cm.

The perceptibility of the layer suggests a likeness to a precipitated layer of a metal. But in that case atoms are formed from the ions by primary discharge and the result is a solid phase with entirely different properties.

In the case of a simple electrolysis the amount of material deposited, A , in proportion to the current I is given by the constant ratio of weight and charge of the ion concerned. In the case of electrophoresis however this "equivalent weight" is a factor determined by the incidental state of charge of the colloid and also by the part played by the particles in the total charge transportation, thus by their mobility u and the sum of the degrees of mobility of all charge carriers, all multiplied by the respective concentrations. Generally, when c is the concentration of the suspended material, the amount in weight passing through the cylindrical shell per unit of time at a distance r from the axis is equal to

$$A = 2\pi l r c u F.$$

Further, according to formula (2):

$$I = 2\pi l r \gamma F,$$

so that $A/I = cu/\gamma$, where $u = \epsilon\zeta/4\pi\eta$.

From this formula it appears, as already observed by Hamaker ⁹⁾, that the amount deposited per unit of time is proportional to:

- 1) the mobility u of the particles, a quantity which characterizes the suspension used;
- 2) the concentration c of the suspended particles;
- 3) the current strength I , which in turn is proportional to the surface $2\pi rl$ of the electrode.

Further the quantity deposited is inversely proportional to the conductivity γ of the liquid. It is therefore of importance to avoid as far as possible any excess of electrolyte — i.e. ions other than

⁹⁾ H. C. Hamaker, Formation of a deposit by electrophoresis, Trans. Faraday Soc. 36, 279-287, 1940.

those belonging to the particles and their counterions — without, however, reducing too much the charge on the surface of the particles (influence on ζ !).

When preparing suspensions of, for instance, ZrO_2 , ThO_2 or Al_2O_3 , the powder is often boiled with hydrochloric acid in order to increase the number of ionized groups in the surface. This has to be followed by a thorough washing out of the excess of electrolyte.

In the foregoing we have seen how, in the case of suspensions of the type represented by curve *b* in fig. 4, a compact deposit is formed. With suspensions of the type *a*, where the particles do not fall into a potential trap — thus very stable suspensions —, it may be expected that after the disappearance of the electric field the particles will move away from each other again. And indeed in such a case it is sometimes seen that the layer gradually runs off the electrode in the form of thick drops. In other cases, however, the internal friction in the layer is so great that, owing to evaporation of the solvent, a certain firmness is reached before any noticeable change takes place. Generally speaking, therefore, both suspensions of the type *a* and those of the type *b* are suitable for electrophoretic coating.

Other factors playing a part in electrophoretic coating

Suppression of the formation of gases

One might ask why preference is not always given to aqueous suspensions when a high degree of stability is required, considering that in these systems the double layer is developed better than in alcohols or acetone, media which were mentioned at the beginning of this article.

It appears, however, that in aqueous media, in the presence of the necessary field strength, electrolytic decomposition causes a very troublesome development of gas, which leads to a pitted layer and may even render deposition quite impossible. The organic liquids mentioned, while still having sufficient polarity, have the advantage that they act at the same time as a depolarizer, that is to say, by chemical reaction they are able to suppress the development of both H_2 and O_2 .

But even when organic media are used, in spite of the low degree of solubility of most salts, the coating may be pitted if too much electrolyte has been added (e.g. to ensure stability).

Drying, adhesion and shrinkage

Another advantage of organic solvents is the

fact that they evaporate quickly, so that within a few seconds of the coated object being removed from the bath the layer already has a certain degree of firmness.

A question of technical importance is whether the layer shrinks in the process of drying and whether such shrinkage takes place uniformly or is accompanied by cracking. Cracks arise from the action of the surface tension of the liquid in the capillary cavities of the layer.

With a view to lending more strength to the layer and also to prevent cracking, in many cases a binder is added to the suspension, e.g. a nitrated cellulose, which makes it much easier to handle the layer. At the same time this ensures good adhesion of the layer to the carrier. For the sake of simplicity this adhesion has not been dealt with as a separate problem in the foregoing considerations. Actually there is a difference compared with the mutual adhesion of the particles, but it is only by way of exception that special measures are called for.

Structure of the layer

In point of fact the firmness of the layer, and thus also shrinkage, depends upon the manner in which the particles are packed. It has already been explained at length how a stable suspension yields a closely packed deposit. Now the possibility is not precluded that in the event of the field strength being too high the particles may not have time to arrange themselves in this favourable position but are prematurely stacked one upon the other in the minimum F , as a result of which the structure of the layer will be of a flocculated type.

In some cases the structure of the layer can be influenced by increasing the field strength, and thus the forces acting upon the particles in the layer, while the layer is being formed. As we have seen when discussing fig. 9, curve 2, the field strength in the layer increases when the electrode voltage is kept constant. If the field strength is to be increased still more then the voltage has to be raised while the layer is being formed.

Since the resistance of the bath increases with the thickness of the layer formed, it can be arranged for this to take place automatically by keeping the current in the bath constant instead of the electrode voltage. The potential variation in the bath will then be as represented in fig. 9, curve 3, from which it is seen that the field strength in the layer increases still more than is the case when keeping the voltage constant. The current can be kept constant by including the bath in the anode circuit of a radio valve with a flat I_a - V_a -characteristic.

Applications

The investigations that led to this new insight into the problem as outlined in the foregoing, and whereby theory and practice have benefited each other, have made a dependable application of electrophoresis possible. Some examples will now be given.

In the preserves industry the tin cans used are enamelled on the inside by the electrophoresis process¹⁰). The cans are filled with a negative emulsion formed by the dispersion of the enamel with the aid of ammonia. The contents of the can are brought in contact with a central cathode, while the can itself serves as anode. After current has passed

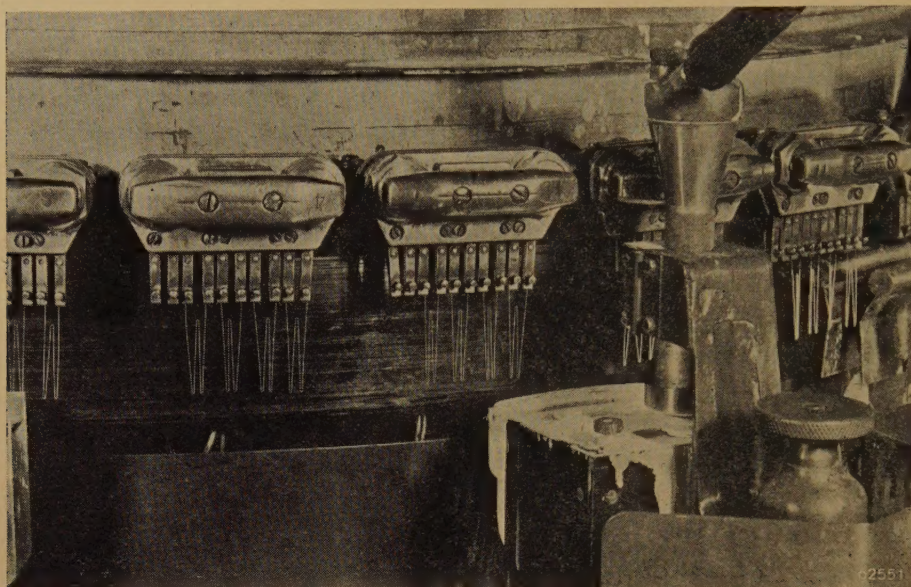


Fig. 10. The electrophoretic coating of filaments with aluminium oxide. The filaments, fixed in holders, are transported, by a turntable rotating step for step, over a tank containing the suspension. The tank is raised until the filaments are immersed, whereupon the voltage is automatically applied for the correct length of time, after which the tank is lowered. The coated filaments are then transported further into a narrow slot (on the extreme right of the photograph) where the first drying is accelerated by a current of air. In the further processing the filaments are gradually heated until the layer is sufficiently dried. This photograph was taken just at the moment that the filament holders were moved along.

In *fig. 10* a machine is illustrated as used for the electrophoretic coating of filaments with an insulating material, mostly aluminium oxide. These filaments are used for the indirect heating of oxide-coated cathodes and are shown in *fig. 11* before and after the coating.

Electrophoresis is often also employed in the manufacture of these cathodes themselves, namely for coating the metal with $\text{BaSr}(\text{CO}_3)_2$. In both cases the coating has to be further processed to make it suitable for its purpose. The Al_2O_3 is heated so as to sinter it into a firm mass. In the evacuating of the radio valve the carbonates are decomposed and thereby the oxides are formed, which at an elevated temperature emit electrons.

Another application of electrophoretic coating is found in the rubber industry, where the emulsion (latex) is deposited upon a surface and the layer is then vulcanized.

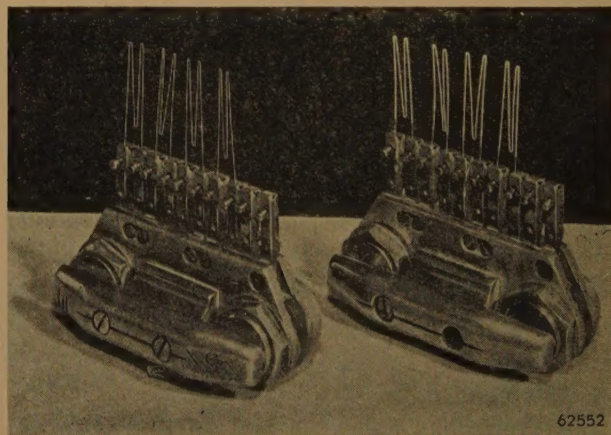


Fig. 11. Two holders with filaments, on the left before coating, on the right coated.

¹⁰) C. G. Sumner, The anodic deposition of oleo-resinous lacquers, *Trans. Faraday Soc.* **36**, 272-278, 1940.

through for a few seconds the can is emptied and rinsed out. The inside of the can is then found to be covered with a milky and strongly adhering layer of emulsion, which after drying and further treatment in a furnace has the appearance of a normal coating of lacquer. The remarkable feature about this application is that a tough liquid, difficult to handle in itself, is precipitated onto the metal from a thin, easily flowing liquid.

Summary. In the electrophoretic method of coating, microscopically small particles are deposited from a suspension onto the electrode by means of an electric field. The possibility of obtaining a good layer is closely related to the stability of the suspension used, which in turn is determined by the nature of the medium and of the substance suspended. The formation of the layer is further influenced by the shape of the electrodes, the voltage applied, the conductivity and the depolarizing power of the medium, whilst rapid evaporation of the solvent is a favourable factor.

Electrophoretic coating is applied, *inter alia*, on a large scale in the manufacture of cathodes for radio valves.

ABSTRACTS OF RECENT SCIENTIFIC PUBLICATIONS OF THE N.V. PHILIPS' GLOEILAMPENFABRIEKEN

Reprints of these papers not marked with an asterisk can be obtained free of charge upon application to the Administration of the Research Laboratory, Kastanjelaan, Eindhoven, Netherlands.

1944*: H. B. G. Casimir: De invloed van magnetische en elektrische eigenschappen van de atoomkernen op de energieniveaux van atomen en moleculen (Ned. T. Natuurk. **16**, 198-206, 1950, No. 9). (The influence of nuclear magnetic and electric moments on the energy levels of atoms and molecules; in Dutch.)

This paper discusses the influence of the dimension of the nucleus (isotopic shift), the influence of nuclear magnetic moments and of nuclear electric quadrupole moments on the spectra of atoms and molecules.

1945: W. J. Oosterkamp: The applications of Geiger counters in X-ray diffraction (Trans. Instruments and Measurements Conference, Stockholm 1949).

Report on instrumental research carried out by W. Parrish and others, Philips Laboratories Inc., Irvington on Hudson, N.Y., U.S.A., and on the author's considerations regarding accuracy in the measurement of strong lines and the detection of weak lines. Some information is given about a high-angle spectrometer and instructional applications of counter tubes.

1946: W. J. Oosterkamp: Design and applications of a dynamic electrometer (Trans. Instruments and Measurements Conference, Stockholm 1949).

Description of an instrument for measuring small direct voltages with high impedance. The voltage to be measured is converted into an alternating voltage by means of a capacitor the capacitance of which varies periodically as a function of time.

This instrument serves for the measurements of α , β and γ radiation, dosimetry of X-rays and ultra-violet radiation, the testing of insulating materials, the measurement of p_H values, etc. (see Philips Techn. Rev. **10**, 338-346, 1948).

1947: N. W. H. Addink: A possible correlation between the zinc content of liver and blood and the cancer problem (Nature **166**, 693, 1950, Oct. 21).

The zinc content of various human tissues and blood has been determined spectrochemically. In the presence of malignant growth the blood has been found to contain $16 \times 10^{-4}\%$ of zinc (average of 6 determinations, S.D. of average $6 \times 10^{-4}\%$) as against $7 \times 10^{-4}\%$ (6 determinations, S.D. of average $1 \times 10^{-4}\%$) in normal cases and $12 \times 10^{-4}\%$ (7 determinations, S.D. of average $1 \times 10^{-4}\%$) in the case of non-tumorous disease, whilst in liver tissue with malignant growth $75 \times 10^{-4}\%$ (6 determinations, S.D. of average $12 \times 10^{-4}\%$) has been found, as against $53 \times 10^{-4}\%$ (7 determinations, S.D. of average $5 \times 10^{-4}\%$) in the case of non-tumorous disease.

R 141: A. van Weel: A comparison of the bandwidths of resonant transmission lines and lumped LC circuits (Philips Res. Rep. **5**, 241-249, 1950, No. 4).

In the design of resonant circuits for very-high frequencies either LC circuits with lumped elements or $\frac{1}{4}\lambda$, $\frac{1}{2}\lambda$ or $\frac{3}{4}\lambda$ transmission lines can be employed. The ratio of the bandwidths obtainable with either type of circuit has been calculated and found to depend on the product $\omega_0 Z_0 C$ (ω_0 = resonance frequency; Z_0 = characteristic impedance of the line;

C = terminal capacitance). The bandwidth of transmission lines used as circuit elements is always smaller than that of an LC circuit; the longer the line, the smaller the bandwidth. For a short-circuited $\frac{3}{4}\lambda$ line the difference is a factor 4 at least. The bandwidth of $\frac{1}{2}\lambda$ and $\frac{3}{4}\lambda$ lines can be increased by introducing discontinuities in the characteristic impedance at certain points along the line. In this way the bandwidth of these lines may be made equal to that of a $\frac{1}{4}\lambda$ line. A qualitative explanation of these effects is given; this explanation holds also for cavity resonators.

R 142: W. Ch. van Geel and A. J. Dekker: Etude sur les condensateurs électrolytiques à courant alternatif (Philips Res. Rep. 5, 250-261, 1950, No. 4). (Study on electrolytic capacitors with alternating current; in French.)

This article deals with electrolytic capacitors for alternating voltages, consisting of two plates of aluminium both covered with a layer of aluminium oxide and placed in an electrolyte. The properties of this system have been studied, special attention being paid to the potential differences between the electrolyte and the plates.

R 143: H. Dormont: Etude rhéographique des champs laplaciens à structure hélicoïdale (Philips Res. Rep. 5, 262-269, 1950, No. 4). (Study of laplacian fields of helicoidal structure by means of the electrolytic tank; in French.)

Two different methods are indicated for determining equipotentials of a helicoidally wound system of conductors by means of the electrolytic tank.

R 144: F. L. H. M. Stumpers: On a first-passage-time problem (Philips Res. Rep. 5, 270-281, 1950, No. 4).

This report on the fluctuation problem deals with the probability that a function, starting at a time $t = 0$ from its average value E_0 , will never have passed a value E_1 during the time interval $(0, t_1)$. This probability is calculated (a) from the Fokker-Planck equation with suitable boundary conditions and (b) from an integral equation derived by Schrödinger.

R 145: J. H. van Santen: Order-disorder for Coulomb forces (Philips Res. Rep. 5, 282-287, 1950, No. 4).

According to order-disorder theories based on nearest-neighbour interaction, above the critical temperature at which long-range order is destroyed only little short-range order is left. From experimental facts (e.g. melting phenomena and order-disorder phenomena in ferrites) it is concluded that, in the case of Coulomb interaction, above the critical temperature a much larger quantity of short-range order, and a corresponding larger energy of order persists. With the aid of Van der Waerden's low-temperature method it is made plausible that in the case of Coulomb forces, long-range order is much more easily destroyed for equal energy differences between the completely ordered and disordered situations than for nearest-neighbour forces.

R 146: W. Nijenhuis: Impedance synthesis distributing available loss in the reactance elements (Philips Res. Rep. 5, 288-302, 1950, No. 4).

This paper deals with two-pole synthesis of networks in which the elements possess maximal losses. It is shown how certain difficulties arising from mutual inductances can be overcome by making use of a paper published by Bott and Duffin. In a subsequent section means are indicated how to introduce losses in coils, e.g., skin effect or eddy-currents losses. A numerical example is given in the appendix.

R 147: A. J. Dekker and W. Ch. van Geel: Les propriétés redresseuses du système $\text{Al-Al}_2\text{O}_3$ -électrolyte soumis à une tension alternative (Philips Res. Rep. 5, 303-314, 1950, No. 4). (Rectifying properties of the system $\text{Al-Al}_2\text{O}_3$ -electrolyte with alternating voltage; in French.)

The $\text{Al-Al}_2\text{O}_3$ -electrolyte system is a rectifier for alternating current. The article deals with the current-voltage characteristic of this system, mainly in the forward direction. A simple experiment shows that there is a considerable difference between the static and the dynamic response. A method is described for measuring the dynamic characteristic without any interference from the capacitive current due to the capacitance of the system. It appears that the characteristic in the forward direction shows a loop. Some properties of this loop are considered.